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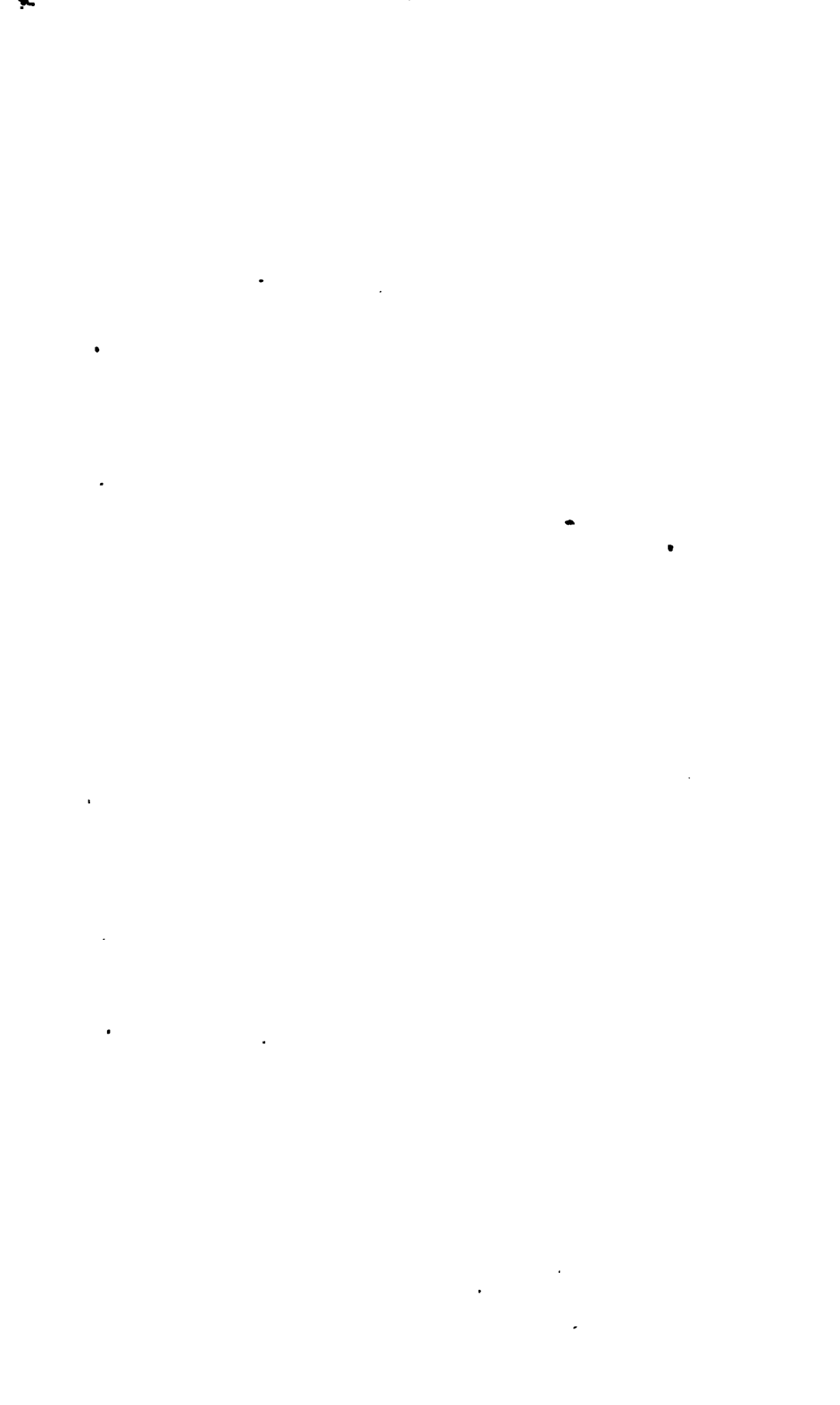
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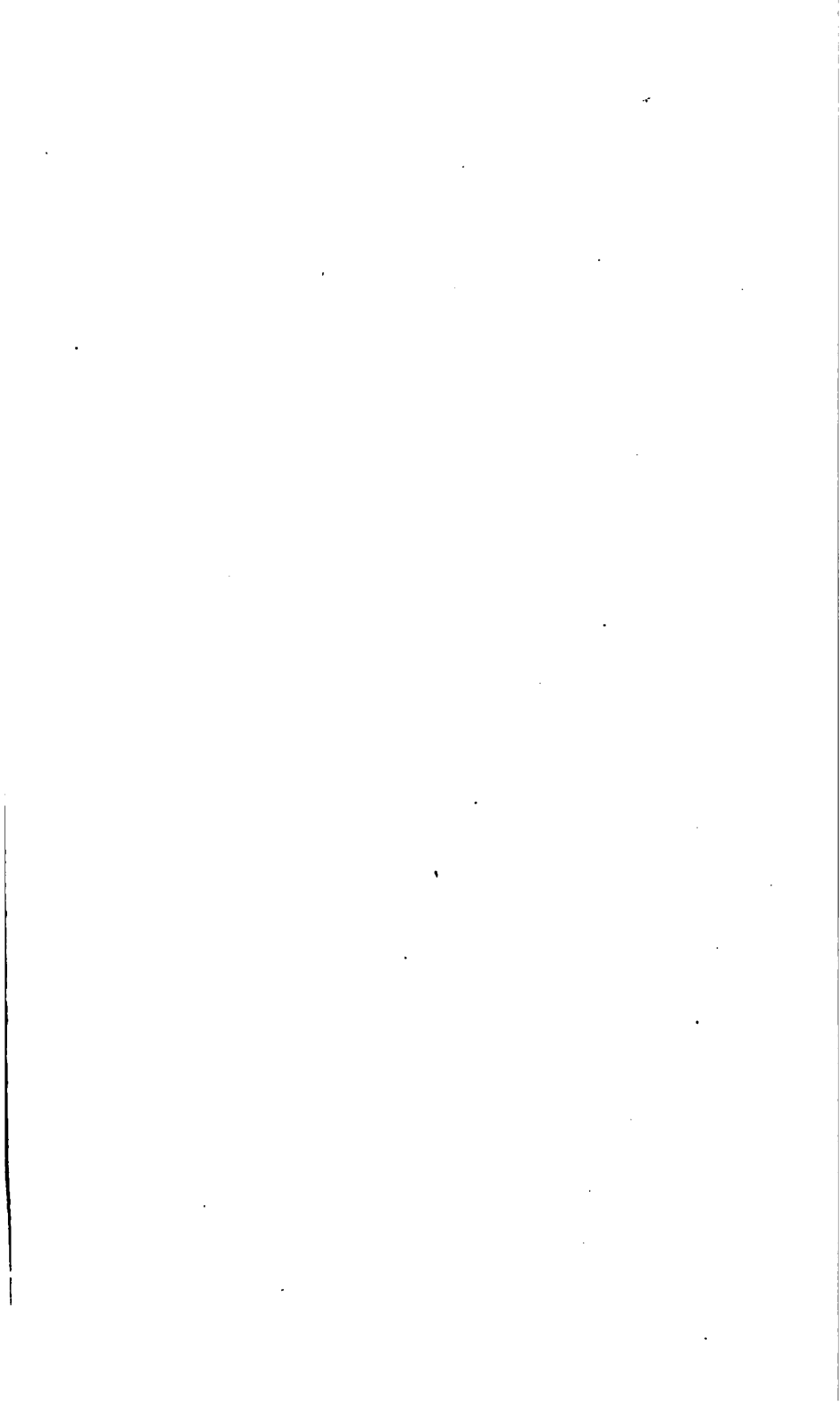
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A
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OF
SULPHURIC ACID AND ALKALI,
WITH THE
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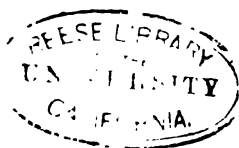
BY

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(FORMERLY MANAGER OF THE TYNE ALKALI-WORKS, SOUTH SHIELDS).

SECOND EDITION, REVISED AND ENLARGED.

VOLUME I.
SULPHURIC ACID.



LONDON:

GURNEY & JACKSON, 1 PATERNOSTER ROW.

(SUCCESSORS TO MR. VAN VOORST.)

MDCCCXCI.

TP201
L3
1391
v.1

48529



PRINTED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

Perseus

P R E F A C E

TO VOLUME I. OF THE FIRST EDITION.

THE present treatise is intended to supply various wants, and, accordingly, appeals to various classes of readers. In the first place, it gives a scientific description of all the substances occurring in the manufacture of sulphuric acid, alkali, and bleaching-powder, either as raw materials or finished products, according to the most recent statements, and thus saves the reader the trouble of collecting the latter for himself whenever he stands in need of them. Secondly, it is intended as an aid in the study of technical chemistry, by giving a complete description, both technical and theoretical, of all the processes occurring in this series of manufactures. Its third and principal object is to give to practical manufacturers both complete and reliable information upon all the apparatus and processes which have come under the author's notice, and thus to enable them to know what has been done in this field beyond the range of their own personal observation.

These objects, especially the third, could not be accomplished without treating the matter in question far more in detail and more in the style of a monograph than has been hitherto attempted. Much space is taken up by the discussion of the innumerable publications, in the English, German, and French

languages, referring to this industry; but even more space was required for the faithful rendering of the author's personal observations and experiences. His own practice of eleven years in the North of England has been supplemented by numerous visits to the other alkali-manufacturing districts of Britain, and to those of Belgium, France, Germany, and Austria. The author's present position as Professor at a technical High School enables him to state frankly what he knows and what he has seen, since he can expect no benefit whatever from keeping any thing back. In his visits he has, of course, been favoured with some confidential communications, which he is not at liberty to reproduce here as he received them; but in every case he has obtained permission to make use of the *substance* of such communications for this treatise, and in the vast majority of cases no restraint whatever has been placed upon him. The author takes this opportunity of publicly thanking the many owners, managers, and chemists of alkali-works who have assisted him in his efforts to make this treatise a thoroughly practical and, above all, a trustworthy book of reference.

The British reader will in this book find the description of many apparatus and processes, and of a large number of facts, partly published abroad, partly never published as yet, but all of them comparatively or almost entirely unknown in his country. But this has not been done to the exclusion of the British styles of working and of the inventions made here, which, on the contrary, form the groundwork of the whole treatise, since the author's personal working experience was gained in England. But it would have ill suited his purpose if he had confined himself to describing his own experience, even when coupled with his notes of what he had observed on his visits elsewhere; he has ransacked the chemical and technical literature, and has not scrupled to mention

nearly every thing, of course very briefly, which he has found bearing upon his subject. This seemed to be unavoidable; for under different circumstances the employment of different processes is not merely permissible, but frequently imperative. Even from decidedly antiquated processes the modern manufacturer may derive suggestions for fresh improvements. It was not very easy to marshal the enormous array of facts thus accumulated, without fatiguing the reader and enhancing the difficulty of studying the book; but the author has endeavoured to accomplish this task, by giving decided prominence to the processes now in general use, and grouping the others around them, appending critical remarks as to their practicability, wherever this was possible. It cannot be fairly expected that in all and every case he should have succeeded in discriminating the wheat from the chaff; some of the processes recommended by him may in the meantime have been replaced by better ones; there will be hardly any larger manufactory which does not in particular points exhibit some improvements upon the apparatus and processes as described here; but the author believes he is not mistaken in asserting that he has missed nothing of *importance*, and that, looking at the very large store of facts offered by him, even the most experienced manufacturer might derive valuable information from this treatise. Without this conviction the author would not dare to come before the public with a work pretentious by its very size.

The illustrations are very numerous, to a great extent from working-drawings, nearly all drawn to scale, and with such details that furnaces and other apparatus can be constructed from them without any further assistance. Many of these are obtained by the favour of some of the largest and best alkali-makers; and they are all the more valuable, as only the most approved forms of apparatus have been selected.

Whatever in this book is taken from previous publications is nearly always quoted, with chapter and section, or volume and page; so that the studious reader may verify it or pursue the subject further. The remainder, so far as it is not common property, is taken from the author's own observations, at the works formerly managed by himself or elsewhere.

The Polytechnic School, Zurich,

April, 1879.

P R E F A C E

TO VOLUME III. OF THE FIRST EDITION.

IN presenting this third and concluding volume of my Treatise to the public, I would first of all return thanks for the numerous expressions of appreciation, printed, written, and verbal, which I have received with respect to the first two volumes.

No one can be less blind than myself to the many shortcomings of my work ; but those communications seem to prove that my hope of doing something useful in the cause of chemical industry has not been altogether unwarranted. It could hardly be expected that my aim, to give a complete record of the theoretical and practical part of my subject, should be absolutely attained. For one man, even aided by so many kind counsels as I have been, it is hardly possible to gain cognizance of every thing which has been done and is doing in hundreds of vitriol- and alkali-works in all civilized countries ; but I have tried to approach to this as nearly as practical ; and if I may believe my critics, nothing of any importance has been omitted.

In this respect my book differs greatly, and designedly (whether to its advantage or not it is not for me to say), from some others which have appeared almost simultaneously with the first two volumes of my Treatise. Those other books aim at nothing but

giving an accurate description of the present style of making sulphuric acid and alkali in England ; and they leave the chemistry of the subject almost totally aside. My Treatise differs from this in several respects. First, it gives a detailed chemical description of the raw materials, intermediate and final products, of the modes of testing and so forth, supplemented by numerous tables of solubilities, densities, &c. ; and it also enters very fully into the theory of all the processes concerned, accurately citing all papers on the subject, so that the reader can go to these for further elucidation. I am quite aware that a treatment of this kind will appear lengthy and superfluous to some readers, who look into this book merely for " practical " hints. In this respect they will not, I trust, be disappointed either ; but I make bold to say that they would do very well not to despise the scientific part, the purely chemical detail, of this work. After all, our subject belongs to the domain of *Chemistry*, and the times are far behind us when, in the manufacture of chemical products, the practical man with his rule of thumb could look down upon the chemist in the laboratory—who, in the former's idea, was at best only good for testing the materials, but whose interference with the works would invariably cause mischief. That this was true to some extent, and still is so, where the chemist attempts to transfer his ideas into practice in a crude state without sufficient practical experience, nobody can possibly deny. But does the " practical man " on his part make no mistakes ? Have not untold sums been wasted in futile " inventions " and " improvements " merely because " practical " inventors lacked a scientific knowledge of their subject ? Probably very much larger sums have been lost in this way than by the deficiency in practical experience of " theoretical " inventors, for the simple reason that the latter class of inventors generally have not so much means at command as the former.

It is a mere truism that theory and practice should always go hand

in hand ; but it must nevertheless be inculcated over and over again, as would appear from the fact that several costly books on, perhaps, the most important branch of chemical industry have just been published with next to no chemistry in them. And to what consequences does this neglect of a scientific treatment of practical subjects lead ? The author may be pardoned for illustrating this from his personal experience. A little more than sixteen years ago he left his native country for Great Britain, because chemical industry was too little developed in Germany, and he might justly hope to learn a great deal and find much more scope for himself in that country which he is proud to have made his second home. More particularly the manufacture of sulphuric acid, soda ash, and bleaching-powder was at that time quite insignificant in Germany, and not very considerable in France, as compared with Great Britain ; nor could the technical appliances, the yields, or even the purity of the products in the two former countries vie with those of the latter. How different matters are now is a matter of notoriety. The manufacture of chemicals has made enormous strides forward, both in quantity and quality, in France, and even more so in Germany. Many of the chemicals of these countries outstrip those of English works in purity ; and their plant and their processes are frequently superior to those used in the majority of English works. Everybody knows how this has come about. The foreign chemists and manufacturers have looked all round, not merely in their own countries, but wherever they could find improved methods and apparatus ; and upon the practical knowledge thus gained they have brought to bear the scientific training they had received at their universities and polytechnic schools. Thus they have already, in many fields formerly remunerative to British manufacturers, distanced the latter, immensely aided though these be by their long occupation of the ground and by permanent natural advantages, such as cheapness of coal and freight, superior command of

capital, &c. ; and this is likely to go on to an increasing extent, if many British chemical-manufacturers decline to profit from a scientific study of their respective branches. This is all the less excusable, as England from of old has been a stronghold of scientific chemistry, and can hold its own against the whole world in that respect.

A second difference of my Treatise from others recently published in England is that the experience of other countries is fully drawn upon. I must leave it to competent readers to say whether, even so far as English plant and processes are concerned, any thing of importance to be found in other treatises is not sufficiently described in this book. But the latter is alone in bringing before the English reader in full detail, illustrated by a large number of scale drawings, the modes of manufacture practised in Germany, Austria, France, and Belgium. Some of the English manufacturers have seen the splendid alkali-works existing in those countries; and to their judgment the author confidently appeals for the expedience of devoting so much space to the description of foreign plant and processes.

Perhaps more objections might be raised to the fact that a certain, although not an unduly large, part of this work is devoted to historical notes and to a description of processes which have either been abandoned long since or which have never become practical, and are not likely ever to be so. Nay, I have even attempted to be as complete and exhaustive as possible, mentioning, although briefly, every thing which has come under my notice in studying the literature and the patent-records of various countries. But I trust to be justified in this respect as well. Who is bold enough, in every instance, to decide whether a patent is quite useless and exploded? Do not many proposals which appear impracticable at first sight, or which have been tried and abandoned again, or which have never been tried at all, contain the

germ of much that is extremely valuable? This is best proved by the fact, abundantly illustrated in this book, that there is hardly a single great improvement in industrial chemistry which has not been preceded by many abortive attempts in the same (that is, in the right) direction—abortive merely because not enough patience, capital, knowledge, and practical ingenuity were expended on them. Hence in the ever continuing and ever increasing stream of inventions, a complete record of all that has previously been done, or merely proposed to be done, should be welcome to the would-be inventor. It will guide him, both by suggesting to him ideas and encouraging him to follow up the lines first traced by others in the past, and not less by informing him of the failure of some ideas which he may have conceived for himself without knowing that others had tried them already.

How many patents have been taken out in succession for substantially or completely the same thing! the money and loss of time for which would have been saved if the inventor could have first consulted a treatise like this, which gives to him (as far as the author has been able to do) a succinct report of all that has been done in his branch before, whether patented or not. Moreover, in all cases where it was possible, it is distinctly stated if, and why, a certain process had failed. It is evident that the most laborious study of the English patent-records by itself, infinitely more time though it would take, still would not yield any thing like the same results. No further apology seems needed for this feature of my book.

The Polytechnicum, Zurich,
October, 1880.

PREFACE

TO THE SECOND EDITION.

THE first two paragraphs of the preface to Vol. III. of the first edition are entirely applicable to this new edition ; I cannot but repeat my thanks, both for the great approbation the first edition has met with, and for the exceedingly numerous hints and detailed communications I have received from practical chemists in all parts of the world during the interval which has elapsed since the first edition was published. I trust the new edition bears proof that I have tried to render full justice to those contributions. Some of these have led me to undertake extensive experimental investigations, the results of which are embodied in the present work.

I have endeavoured to keep to the programme sketched in the preceding prefaces. But the mass of new matter which has accumulated in the domain of sulphuric-acid and alkali-making during the last twelve years is so large that it seemed advisable to curtail the merely retrospective portion, which describes apparatus and processes not in practical use now. Undoubtedly a great deal may still be learned from these ; and inventors of new processes will do well to carefully look up everything which has been done before in the same line. With this object I

have in every case, where I have cut down or left out such descriptions, referred to the first edition, so that those who are specially interested in processes formerly used or proposed have their attention drawn to them, and may look them up in the first edition, which, therefore, will always remain useful even to those who possess the new edition. The same has been done with specific-gravity tables and similar matter. Some readers may think that I have omitted matter which would have been better retained in the present edition, whilst others may consider that I ought to have left out much more than I have done; it would evidently be impossible to suit everybody's convenience and ideas in this respect. But all readers will, I hope, approve of my having cut out many pages containing discussions or refutations of views which may now be considered entirely obsolete.

In spite of these omissions, which comprise nearly a hundred pages of text and a large proportion of the engravings, the new first volume is far more bulky than its predecessor. In lieu of 658 pages of text and 309 engravings, we have now 903 pages of text and 374 engravings (more than 150 of which are new). But this does not mean that a corresponding quantity of fresh matter has been simply superadded to the old. Everything has been overhauled; there is hardly a single page as it stood in the first edition; considerable portions of all the chapters, in some cases nearly the whole, have been entirely re-written. This is, in point of fact, a new book, for which the first edition has only served as the principal source of information. I have not scrupled, in some few cases, to contradict statements of "fact" or opinions I had enounced in the first edition, wherever I have improved my knowledge by my own observation, or from information contributed by numerous kind readers and friends. I do not, of

course, apologize for this inconsistency, if anyone chooses to call it so; but I crave kind indulgence for the errors unavoidably still left in my book, for which I am very far from claiming anything like perfection. But, nevertheless, I sincerely hope that this new edition will be found a great improvement upon the first, and that it will prove a useful and trustworthy companion to those concerned with the manufactures here described.

The present volume forms an independent treatise on the manufacture of Sulphuric Acid; a new edition of the other two volumes (Soda and Chlorine) cannot be issued for several years to come.

The Polytechnic School, Zurich,
July, 1891.



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INTRODUCTION.

FORMERLY the term "alkali manufacture" nearly always comprised a cycle of operations, beginning with the manufacture of sulphuric acid and proceeding to that of sulphate of soda (salt-cake), hydrochloric acid, soda-ash (with caustic soda, soda-crystals, &c.), and bleaching-powder. This cycle is not completed in all factories, but frequently (at the present day even more so than formerly) the operation stops at sulphuric acid or sulphate of soda; but we may embrace all this under the general term of "Sulphuric Acid and Alkali Manufacture."

In this wider meaning the products of alkali-making are necessary materials for many metallurgical processes, for the manufacture of artificial manures, soap, fatty and mineral oils, glass, paper, many inorganic and organic colouring-matters (especially nearly all coal-tar dyes), and even of many articles of food,—that is to say, for nearly all branches of manufacturing chemistry. In fact, among all branches of chemical industry the cycle of technical operations connected with alkali-making is preeminent, not merely from the magnitude of the works and the absolute bulk of the raw material used and the quantity produced, but also from the fact that most other chemical products require one or more branches of alkali-making as the conditions of their own existence. It can be truly said that the manufacture of acids and alkali is the foundation upon which the whole chemical industry of our times is built up, and that such industry cannot

be much developed in any country not possessing a flourishing alkali trade, or not being at least specially well situated for buying the produce of the latter. It is thus evident how great is the importance of the alkali trade in its wider meaning to the civilization of mankind, though we should certainly be going too far if we measured, as some have done, the civilization of a country by the development of this special industry.

Formerly the whole cycle of processes here described was intimately connected with the great invention of Leblanc, now just about a century old. Ten or twelve years ago, although the ammonia-soda process had then already more than proved its right to be considered a full success, it had not yet shaken in any tangible way the supremacy of the Leblanc process, at least not in Great Britain. In the latter process the different branches of "alkali-making," mentioned above are connected in such a manner that only under special local conditions can one or more of the principal substances be omitted. Formerly this was the case even less than now, as the competition of ammonia-soda ash has completely altered some of the conditions of trade, making it unremunerative in some cases to convert the sulphate of soda into the carbonate. Thus there exist now many works stopping at the manufacture of sulphuric acid, and others which go as far as sulphate of soda, together with chlorine products; but the majority, at least in this country, proceed still further, going on to the manufacture of soda in its various branches.

The manufacture of *sulphuric acid* is in reality a very large industry, quite apart from its connection with the Leblanc process. Enormous quantities of it are required for the manufacture of artificial manures (fertilizers), and therefore every large manure-works makes its own sulphuric acid. This is done also by the largest sulphate-of-ammonia works, and perhaps in a few other cases. Some works in England, and many on the Continent, make sulphuric acid to a great extent, or even entirely, not for their own use, but for sale. Since this acid is no longer sent out in any considerable quantity in glass carboys, but in

iron tank-waggon, it can be carried to considerable distances at moderate cost.

As sulphuric acid is mostly made from pyrites, its manufacture is intimately connected with the recovery of *copper* from the cinders, in which process iron oxide, silver, and other by-products are obtained.

A very large (formerly even the largest) quantity of sulphuric acid is used up at the works themselves for the manufacture of *sulphate of soda* (salt-cake) and *sulphate of potash*, in which *hydrochloric acid* is a necessary by-product. Sometimes salt-cake is obtained without previously manufacturing sulphuric acid, as a by-product of other manufactures or by the "direct process" of Hargreaves and Robinson. There is only one use of salt-cake on a large scale, except for alkali-making, namely, for the manufacture of glass; but by far the largest quantity of salt-cake enters into the *Leblanc process for manufacturing soda*. This article is mostly the final product, either in the calcined or crystallized or caustic state, and the series of operations is thus brought to a close in this direction.

Hydrochloric acid (*muriatic acid*) is, of course, sold as such to some extent, but in nothing like such large quantities as sulphuric acid, as its carriage is impossible in metallic vessels, and therefore very expensive and troublesome. Most of it is at once, sometimes even without condensation to liquid acid, converted into *chlorine*, which, being a gas, must necessarily be immediately worked up into bleaching-powder or chlorate of potash, or occasionally into other products. The time when the hydrochloric acid was condensed merely to satisfy the exigencies of laws made for protecting the health and vegetation of a neighbourhood, and was then run to waste into the nearest watercourse, is now past, since the process of decomposing salt by sulphuric acid is only profitable if the hydrochloric acid is fully utilized: this acid has thus risen from the rank of a by-product to that of the best-paying principal product.

Recently the conditions of the Leblanc process have been

again changed by the solution of the problem of the *recovery of sulphur* from the alkali waste, and it has now been made into a real cycle, into which common salt and coal enter at one side, alkali and chlorine issuing at the other, whilst sulphur and possibly even lime are made to do service over and over again. This, however, will be made clearer in a later part of this Treatise ; to which we also refer for such general observations as the ammonia process of soda manufacture calls for.

FIRST BOOK.

SULPHURIC ACID.

CHAPTER I.

HISTORICAL AND GENERAL NOTES ON THE MANUFACTURE OF SULPHURIC ACID.

History of the Manufacture of Sulphuric Acid.

ACCORDING to Rodwell ('Birth of Chemistry') it is very probable that sulphuric acid was already known to the ancients; but usually its first, although indistinct, mention is ascribed to the Arab Geber, who speaks of the "spirit" which can be expelled from alum and which possesses solvent powers. Others give this honour to the Persian alchemist Abu-Bekr-Alrhases, who is said to have died in 940. Vincentius de Beauvais (about 1250) alludes to it; and Albertus Magnus (1193–1280) speaks of a *spiritus vitrioli Romani*, which can only have been sulphuric acid; his "sulphur philosophorum" is the same thing.

With all distinctness Basilius Valentinus, in his 'Revelation of the Hidden Manipulations,' describes its preparation from calcined copperas and silica, and, in his 'Triumphal Car of Antimony,' also its preparation by burning sulphur with saltpetre (Kopp, 'Geschichte der Chemie,' iii. p. 303); but he took the two for different substances.

Gerhard Dornæus (1570) described its properties accurately; Libavius (1595) recognized the identity of the acids from different processes of preparation; the same was done by Angelus Sala (1613), who pointed out the fact, which had sunk into oblivion since Basilius, that sulphuric acid can be obtained by burning sulphur in moist vessels (of course with access of air); after that time it was prepared by the apothecaries in this way. An essential improvement, viz. the addition of a little saltpetre, was introduced in 1666 by Nicolas le Fèvre and Nicolas Lémery. This caused a sort of manufacture of vitriol which is said to have been introduced into England by Cornelius Drebbel: this only is certain—that a quack doctor of the name of Ward first carried

on sulphuric-acid making on a large scale at Richmond near London, probably a little before 1740. Ward employed large glass vessels up to 66 gallons capacity, which stood in two rows in a sand-bath, and which were provided with horizontally projecting necks; at the bottom they contained a little water. In each neck there was an earthenware pot, and on this a small red-hot iron dish, into which a mixture of one part saltpetre and eight parts of brimstone were put; then the neck of the bottle was closed with a wooden plug; on the combustion being finished, fresh air was allowed to enter the vessel, and the operation was repeated till the acid had become strong enough to pay for concentrating in glass retorts.

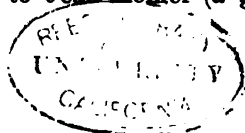
Ward called the product "oil of vitriol made by the bell" (already Basilius Valentinus had used the expression "*per campanam*" in this sense), in order to distinguish the spirit of vitriol made from brimstone from that distilled from copperas, the latter having been made on a kind of manufacturing scale in England previously: an exact description of this is given by J. C. Bernhardt in his '*Chemische Versuche und Erfahrungen*,' 1755. Ward's process, troublesome as it is, reduced the price of the acid from 2s. 6d. per ounce (the price of the acid from copperas or from burning brimstone under a moist glass jar) to 2s. per lb.

An extremely important improvement in this process was the introduction of the *lead chambers*, which by general consent is ascribed to a Dr. Roebuck of Birmingham, who in 1746 erected such a chamber 6 feet square, and in 1749, in partnership with Mr. Garbett, built a factory, founded thereon, at Prestonpans in Scotland, in order to supply acid for the bleaching of linen. The mixture of brimstone and saltpetre in the above proportion was put into small iron waggons which were run into the chamber on a railway: the chamber was closed, and the process carried on intermittently in this way.

Soon other works followed at Bridgenorth, and at Dowles in Worcestershire, where the chambers were already made 10 feet square; in 1772 there was a factory erected in London with 71 cylindrical lead chambers, each 6 feet diameter and 6 feet high. In 1797 there were already six or eight works in Glasgow alone. According to the statements given in Mactear's '*Report of the Alkali and Bleaching-Powder Manufacture in the Glasgow District*' (p. 8), the acid at that time cost the Glasgow manu-

facturers £32 per ton, and was sold at £54. At Radcliffe, near Manchester, it cost, in 1799, £21 10s. per ton, without interest on capital. In the latter place there were six chambers 12 feet long, 12 feet wide, and 10 feet high, with roofs like those of houses, and valves opened between each operation; on their bottom there were 8 or 9 inches of water; every four hours there was burnt in each chamber a mixture of 1 lb. saltpetre and 7 lb. brimstone on iron shelves, of which each chamber contained four, 4 inches distant from one another. The shelves were made of very thin iron, in order to get heated very quickly, and rested on iron frames, by means of which they could be slid in and out; a quarter of an hour before each operation the valves and doors were opened in order to allow air to enter. Thus, weekly, 1386 lb. of brimstone and 198 lb. of saltpetre were burnt, yielding 1800 lb. of oil of vitriol—that is, 130 per cent. of the sulphur with a consumption of 14·28 per cent. saltpetre on the same. In six weeks the strength of the acid only attained 1·250 sp. gr.; it was thus run off and concentrated up to 1·375 sp. gr., in which state it was used and sold. At Prestonpans, in 1800, only a yield of 111 per cent. on the sulphur was attained, with a consumption of 13 per cent. saltpetre on the brimstone; in 1813 there were in that place 108 chambers of 14 feet length, 10 feet height, and 4½ feet width. In 1805 there existed at Burntisland a factory with 360 chambers of a capacity of 19 cubic feet each.

In the meantime the first lead chamber in France had been erected at Rouen by Holker in 1766. In 1774, in that place, on the advice of De la Folie, an important improvement was introduced, viz. the introduction of steam into the chambers during the combustion of brimstone. In 1793 Clément and Desormes showed that the acid-chambers can be fed by a *continuous* current of air, by which a great deal of saltpetre could be saved. They showed that the oxidation of sulphurous acid takes place to the extent of nine tenths at the expense of atmospheric oxygen, and that the saltpetre only plays the part of intermediary between the air and the sulphurous acid. By this the modern theory of the essence of the sulphuric-acid-making process was established; but it took a remarkable long time before the difficulties were overcome which stood in the way of introducing the continuous system into practice. Usually the introduction of the continuous burning of brimstone is ascribed to Jean Holker (a grandson of



the first Holker), in 1810; but, according to Mactear, a continuous system had been introduced at St. Rollox, at least partially, already in 1807: steam was first introduced there in 1813 or 1814.

In Germany the first lead chambers seem to have been those at Ringkuhl, near Cassel. One of the oldest chambers was that erected by a Dr. Richard at Potschappel near Dresden in 1820; as he had no plumber at his disposal, he had to solder the chamber himself with soft solder and a smoothing-iron (Bode, in his translation of H. A. Smith's 'Sulphuric Acid Manufacture,' p. 96). This chamber was still charged intermittently, 100 lb. of brimstone yielding only 150 lb. of vitriol. It must therefore be said that the industry of vitriol-making was very late in gaining a footing in Germany.

Kestner, of Thann in Alsace, was the first to collect the products of condensation at the chamber-sides in order to regulate the working of the chambers thereby. This innovation was at once considered of such importance that Kestner was called to Glasgow in order to introduce his plan into Tennant's works.

At last, in 1827, Gay-Lussac's condensing-apparatus for the nitre-gas escaping from the chambers was invented: at Chauny this apparatus was erected in 1842, at Glasgow in 1844. But we have now come so near the present time that we may conclude the historical part of our task.

General Principles of the Manufacture of Sulphuric Acid.

Sulphuric acid can be obtained on a large scale in one of two ways—viz., first, by burning brimstone or sulphides into sulphurous acid and further oxidizing the latter, or, secondly, by decomposing natural or artificially prepared sulphates. The latter process, apart from several proposals so far not carried out practically, only serves for making fuming oil of vitriol, which will be treated of hereafter; by far the greater portion of sulphuric acid is obtained by the former process, which will occupy us in the first instance. We shall, at first, only describe those apparatus and processes which actually serve for manufacturing on a large scale; and we shall close by mentioning the alterations which have merely remained as proposals, as well as the processes founded on totally new principles.

By the *combustion of sulphur*, either free (as brimstone) or com-

combined with metals or with hydrogen, *sulphurous acid* (sulphur dioxide, SO_2) is always formed at first. Sulphuretted hydrogen, even when mixed with as much as 70 per cent. of inert gases (nitrogen), can be lighted like illuminating gas and continues burning without any difficulty, aqueous vapour being formed at the same time as SO_2 . Brimstone ignites in the air at a temperature rather below 300°C .; and when once it has begun to burn, the heat generated suffices to raise the whole of the sulphur to the point of ignition, provided that sufficient air be present. A number of metallic sulphides behaves similarly: the most important of these for our purpose is the iron bisulphide, FeS_2 ; but here special precautions must be taken, so that the whole mass may be completely burnt (roasted). In both cases, along with sulphur dioxide, SO_2 , a little trioxide (sulphuric anhydride), SO_3 , is always formed, and, in the presence of water or steam, also sulphuric acid, SO_4H_2 , more or less diluted with water. Moreover an aqueous solution of sulphurous acid in contact with air gradually changes into sulphuric acid. In both cases it is, of course, the oxygen of the air which converts the SO_2 into SO_3 or SO_4H_2 ; but this reaction at the ordinary or only moderately elevated temperature goes on far too slowly to be applicable for technical purposes. There are two ways of increasing the affinity between SO_2 and O , either in the presence or in the absence of H_2O . One way (which can be employed also in the absence of water or steam) is the employment of porous substances, which condense both the oxygen and the sulphurous acid: the affinity between the molecules thus brought much closer together is increased to such an extent that ultimately they combine chemically, at least partially, and yield sulphuric anhydride or hydrate, according to whether water is present or absent. As such porous substances, pumice, burnt clay, chromium sesquioxide, iron peroxide, cupric oxide, even cotton-wool, have been recommended. The action of these substances, however, which must always be increased by higher temperatures, is so incomplete that they have found no technical application. The case stands rather better with platinum, which, as is well known, exercises an extraordinarily strong condensing power upon gases at its surface, so that, for instance, hydrogen and oxygen can be brought thereby to combine at the ordinary temperature. The more finely divided the platinum is, the larger, therefore, its surface for a certain weight, the more energetically

it acts in that way; and the best results have been obtained with platinized pumice and asbestos. This will be explained in detail with the fuming oil of vitriol: here it may suffice to say that platinum, even in its most finely divided form, cannot form the foundation of a real manufacture of sulphuric acid, and that the only successful way of utilizing it is that of manufacturing sulphuric anhydride.

The second way of making the oxygen of the air better adapted for combining with sulphurous acid is the only one actually employed in the practice of manufacturing sulphuric acid. It is founded on the property of the acids of nitrogen to serve as carriers of oxygen from atmospheric air upon sulphur dioxide and water, the original nitrogen oxide being always re-formed. This process will be explained in detail when we treat of the theory of the formation of sulphuric acid.

We have just seen that the reaction between nitrogen acids and sulphurous acids only goes on in the presence of water; and we must add at once that, in practice, much more water is needed than suffices for the formation of SO_4H_2 ; the sulphuric acid formed is therefore always *dilute*, and must be *concentrated* for most purposes.

For some purposes the acid must also be deprived of certain foreign substances which get into it from the raw materials and the apparatus; and in that case the sulphuric acid has to be *purified*.

Thus our subject subdivides itself into the following headings:—

1. *The generation of sulphurous acid.* Since the respective processes differ very much, both as to apparatus and as to the way of proceeding, we have to distinguish between (a) sulphurous acid from brimstone, (b) from metallic sulphides, (c) from sulphuretted hydrogen.

2. *The conversion of sulphurous acid into sulphuric acid*, which is always done in the so-called lead chambers, where also the introduction of nitric acid and steam, and the recovery of the nitre-gas carried away by the draught, will be described.

3. *The purification.*

4. *The concentration of vitriol.*

5. *The utilization of the by-products.*

All this will be preceded by an examination of the *raw materials* of the sulphuric-acid manufacture, and by an account of the *properties of the oxides and acids of sulphur*.

CHAPTER II.

THE RAW MATERIALS OF THE SULPHURIC-ACID
MANUFACTURE.

1. BRIMSTONE.

BRIMSTONE, owing to its being found in nature in the free state, has been known to mankind since very ancient times. It is hardly necessary to point to its being noticed in the Bible; it is also mentioned several times in the Homeric poems. The Romans evidently obtained it in the same way as is done now, by melting it out of its mixture with marl, &c. The Ancients employed it principally for fumigating purposes, both on account of its disinfecting properties and as a religious rite (compare the well-known passage from the Odyssey, where Ulysses purifies his house after slaying the intruders), but also for many of the uses it is put to in our times, as for cleaning wine-casks, for destroying fungus-growths in vineyards and orchards, for plasters in skin-diseases, for lighting fires and preparing torches, for cementing glass, for bleaching, for "niello" work on metals*.

In modern times brimstone has been used for most of the just-mentioned purposes and for many others; but we are here concerned only with its use for the manufacture of sulphuric acid. Brimstone is undoubtedly the most convenient raw material for this manufacture, and for a long time all the sulphuric acid of commerce was made from it; but its use in this respect has been almost entirely abandoned in most localities, and is not likely to be revived, since iron-pyrites, and more especially that containing a few per cent. of copper, supplies sulphur for the above purpose far more cheaply than natural brimstone ever can do. In spite of this, brimstone is still the principal raw material for the manufacture of sulphuric acid in America (where, however, it has lost its former

* I owe these historical notes to a treatise by Professor Blümner, of Zürich, in the 'Festschrift zur Begrüssung der Philologen-Versammlung' (Zürich, 1887), p. 23 *et seq.*

exclusive sway), and it is also used to some considerable extent in England for that purpose, but very little indeed in other European countries.

A somewhat considerable quantity of brimstone is also consumed in the manufacture of sulphurous acid, principally in order to prepare bisulphate of lime for the manufacture of wood-pulp.

Sulphur is an element whose atomic weight is now assumed to be 32.06 (oxygen = 16). It is very brittle; its hardness is from 1.5 to 2.5 of the ordinary mineralogical scale; its specific gravity is 2.0454. As usually occurring, it is semi-transparent at the edges and of the well-known bright yellow colour, which darkens with an increase of temperature; at -50° it is nearly devoid of colour. Its taste and smell are very slight. It does not conduct electricity, but itself becomes electric by friction; and it is therefore difficult to powder finely, as it adheres to the mortar and pestle.

Sulphur melts at $111^{\circ}.5$ C., and forms a thin, light-yellow liquid, which, on being more strongly heated, becomes darker and thicker; at 250° to 260° C. it is nearly black, and so viscid that it does not run out when the vessel is upset; at a still higher temperature it becomes thinner again, keeping its brown colour; and at 446° C. it boils, forming a brownish-red vapour; but it begins to volatilize before boiling; and its action on silver seems to show that it does so to a slight extent even at the ordinary temperature (unless there is formation of H_2S in this case).

Sulphur exists in different allotropic conditions. That occurring in nature often appears in rhombic crystals, mostly pointed rhombic octahedra, whose physical properties have been described above; this α -modification is also obtained by crystallizing sulphur from its solution in carbon bisulphide. The β -modification is obtained by slowly cooling melted sulphur, and pouring off the liquid portion when another portion has crystallized; it consists of long thin oblique rhombic prisms, belonging to the monoclinohedric system, of a brownish-yellow colour, transparent, spec. grav. 1.982; they gradually pass over into the α -modification, completely so after a few days, even at the ordinary temperature—suddenly by shaking or scratching; the colour then becomes light yellow; and the crystals lose their transparency, but remain as pseudomorphs of the β -sulphur. The sulphur in rolls consists, when fresh, of β -sulphur—after a short time, of α -sulphur. When sulphur has been heated up to the point of viscosity, and

is then poured into very cold water, the γ -modification is formed, viz. amorphous, soft, tough, reddish-brown sulphur, of 1.957 spec. grav.; this also is gradually converted into α -sulphur; but it takes some time before this conversion is complete. The tough state lasts very much longer if resinous substance, iodine, &c. are mixed with the sulphur, even in very small quantity. This modification is partly contained in the "flowers" of sulphur.

Heated in the air to $250^{\circ}\text{C}.$, sulphur inflames and burns with a purplish-blue flame, forming sulphur-dioxide (SO_2), and giving out 2221 metrical units of heat per gram of sulphur. More exactly, according to Thomsen (Berl. Ber. 1880, p. 959), the heat evolved in burning the different modifications of sulphur, expressed in atomic calories, is:—

S (rhombic, octahedric) + $\text{O}_2 = \text{SO}_2 = +71,080$ cal.

— S (monoclinic) . . . + $\text{O}_2 = \text{SO}_2 = +71,720$ cal.

Hence the conversion of 32 parts by weight of monoclinic into rhombic sulphur is accompanied by the evolution of 640 calories. Berthelot, however (Compt. rend. xc. p. 1449), states the figure for octahedric sulphur = +69260 atom. cal. = 2164 gram-calories.

Hydrogen combines with sulphur very slightly at a temperature of 120° , very sensibly so at 200° . On boiling sulphur with water, hydrogen sulphide is evolved and sulphuric acid is found in the residue (Cross & Higgin, J. Chem. Soc. xxxv. p. 249; comp. also Colson, Bull. Soc. Chim. [2] xxxiv. p. 66; Böhm, Jahresb. 1883, p. 225).

Sulphur is insoluble in water, a very little soluble in alcohol and in glycerine, rather more so in essential oils, but easily soluble (excepting the γ -modification) in bisulphide of carbon and in chloride of sulphur.

The sulphur occurring in commerce as *refined sulphur*, in rolls or as "rock-sulphur," is frequently almost chemically pure. "Flowers of sulphur" always contains a little sulphurous acid, also some sulphuric acid, persistently retained in spite of prolonged washing; it owes its greater efficacy against diseases of the vine (oidium) and other cases principally to this property.

O. Roessler (Arch. d. Pharm. 1887, p. 845) states that sulphur in rolls is practically free from acids of any sort. Flowers of sulphur contains a somewhat considerable quantity of sulphurous acid (100 grams up to 3.14 c. c. of SO_2), which may be partially

* Comp. J. R. Hill, Chem. News, 1890, lxi. p. 126.

oxidized to sulphuric acid; thiosulphuric acid is not found in it, but in milk of sulphur (up to 0.15 per cent.).

Natural Occurrence of Sulphur.

Sulphur occurs in nature in very large quantities, both in the free state as brimstone, and in combination with other bodies as sulphides and sulphates. Deposits of brimstone are forming at the present time, especially in volcanic countries, by the decomposition of sulphuretted hydrogen and of sulphurous acid.

Daubrée (Compt. rend. xcii. p. 101) noticed a recent formation of sulphur in the subsoil of Paris, from the action of organic substances on sulphates; and the same action has been noticed in many mineral springs, where it is especially attributed to action of Algæ, such as *Beggiatoa*, *Oscillaria*, and *Ulothrix* (Compt. rend. xcv. pp. 846 & 1363).

But of far more importance are the beds of brimstone deposited in former geological periods. The most important of all are those of Sicily, in the Chalk; next, those in the Romagna and in other parts of Italy. The *Sicilian brimstone-industry* is described in detail by Angelo Barbaglia in Hofmann's Official Report on the Vienna Exhibition, i. p. 144, and by Parodi (Berichte d. deutsch. chem. Ges. 1874, p. 358). According to the latter, the disposable stock of brimstone in Sicily is said to amount to ten millions of tons; so that it would be exhausted about 1950. Other calculations give more than twice that figure. The apparatus for melting the sulphur out of the "sulphur-earth" in Sicily is also described by Barbaglia; we will only mention that the melting has lately been very successfully effected by high-pressure steam, in apparatus quite similar to that of Schaffner, which will be described with the recovery of sulphur from alkali waste.

De la Tour de Breuil (Compt. rend. xciii. p. 456) employs a 66-per-cent. solution of calcium chloride for the same purpose. C. Vincent recommends this process (Bull. Soc. Chim. xl. p. 528).

K. Walter, in Milan, has patented an apparatus for continuously melting out sulphur by combustion of part of the sulphur itself, and converting the sulphur dioxide formed into sulphuric acid in lead chambers (Chem. Zeit. 1886, p. 1199).

The American patents of F. Dickert, Nos. 298,734 and 301,222,

describe an apparatus for melting sulphur, consisting of a jacketed pan connected by a perforated diaphragm with another jacketed pan turned bottom upwards. The melting is produced by means of steam introduced into the jacket.

More recent descriptions of the Sicilian sulphur industry are found in the 'Chemiker-Zeitung' of 1882, pp. 1389, 1405, 1421; also in 'Zeitsch. f. angew. Chemie,' 1890, p. 56, and in the 'Journal of the Society of Chemical Industry,' 1890, p. 118.

The following statistics of the exportation of Sicilian Brimstone is given by A. S. Malcolmson (J. Soc. Chem. Ind. 1889, p. 313):—

Exported to	1883.	1884.	1885.	1886.	1887.	1888.
	tons.	tons.	tons.	tons.	tons.	tons.
United States	96,629	94,929	99,378	98,590	89,419	128,265
France	63,602	65,008	58,264	54,280	56,222	52,083
Italy	66,810	56,292	49,415	48,658	48,997	47,664
United Kingdom	41,788	40,760	33,402	30,236	30,007	35,634
Greece	10,494	7,033	13,664	19,697	18,370	5,800
Portugal	15,298	11,018	17,760	30,943	16,587	15,851
Russia	10,413	12,831	13,420	10,570	13,441	22,043
Germany	7,232	6,622	6,103	8,698	9,700	12,402
Austria	4,915	6,037	5,965	5,800	6,702	8,942
Turkey	3,043	1,285	3,077	4,598	6,238	1,457
Spain	5,242	3,920	2,243	5,890	5,873	3,433
Belgium	7,660	6,793	9,516	6,580	5,318	6,951
Holland	1,256	696	1,237	2,900	1,747	2,793
Sweden	1,010	744	328	1,916	1,169	3,004
South America	710	95
Australia	600	885
Denmark	810	202	464
Total	335,392	314,058	314,582	329,455	311,302	347,775

In 1886 the Sicilian sulphur production amounted to 410,000 tons; there were 630 pits at work, with 52,000 men.

The importation into Germany, according to official sources, was, including refined sulphur, 16,674 tons in 1888, 18,945 tons in 1889.

The average price of sulphur in Sicily itself in 1881 was 115 lire, in 1882 105 lire, in 1887 only 69 lire (say £2 15s.) per ton.

The cost-price by the ordinary calcarone process, according to Parodi, was, in 1875, for 100 kil. brimstone at the mines themselves:—

	frs.
700 kil. sulphur-ore, average quality	4.00
Cost of fusion	0.47
Royalty to the landowners	1.68
	<hr/>
	6.15

or, say, £2 8s. 3d. per ton.

The cost of fusion by steam, without patent royalty, comes to frs. 1.87 per 100 kil. of sulphur, or frs. 1.40 more than in the calcarone process; but the yield from the ore is about 30 per cent. more in the former than in the latter process, so that the advantage would be still in favour of the former even with coals at 46s. per ton.

Northern Italy formerly yielded a very large quantity of brimstone, especially the Romagna; but many of the beds are now exhausted, and the production is slowly receding, from 23,274 tons in 1886 to 21,663 tons in 1887 (details in the *Chem. Zeit.* xii. p. 1659; abstr. *J. Soc. Ch. Ind.* 1889, p. 142). The whole of this brimstone is used for inland consumption, as a remedy against the vine disease.

Sulphur containing *selenium* is found in the Lipari Islands and near Naples, but not in quantity.

In many other parts of the world deposits of sulphur have been found, and have been sometimes declared to be very important; but hitherto these sulphur-mines have not made any sensible impression on the brimstone trade, of which Sicily has still almost the monopoly. The more important of these sulphur-mines are the following:—

In *Poland*, at Swoscowice near Cracow, an old sulphur-mine exists which for some years was carried on with great vigour, the sulphur being extracted from the marl by means of carbon disulphide. This bed is now practically exhausted, and the mine has ceased working (*Wagner's Jahresb.* 1878, p. 333, 1879, p. 272; *Fischer's Jahresb.* 1885, p. 204). Not far from this mine are the beds of sulphur-marl at Pschow and Kokoschütz, near Ratibor, in *Upper Silesia*, which are up to 20 feet thick (*Chem. Ind.* ii. p. 136). They are more minutely described in *Fischer's Jahresb.* 1882, p. 233, where also the various processes employed for extracting the sulphur are criticised; but not one of them has

answered there except the employment of disulphide of carbon : a considerable quantity of sulphur can be obtained in this way.

Sulphur has also been found in quantity in the *Stassfurt* deposits (Pfeiffer, D. chem. Ges. Ref. 1890, p. 192).

Several occurrences of sulphur are known in *Russia*. A new bed of brimstone has been found by Gluschkoff in the Astrachan Government, on the east bank of the Baskuntschak salt-sea; it is a mixture of a sandy rock with 30 to 35 per cent. of pure sulphur (Fischer's Jahresb. 1884, p. 264). In West Siberia considerable beds of sulphur are said to exist.

In the Vistula district a sulphur-bed is being worked at Czarki, which in 1883 yielded 60,000 pud.

In the sandy steppe of Karakum a large number of conical hills have been discovered consisting of sulphury rock of 50 per cent. (Chem. Zeit. 1884, p. 478).

In the north of the Caucasus, in the Grodno district, sulphur has been found by Baron Heyking (Chem. Zeit. 1887, p. 1620).

Rich sulphur-mines are found in *Andalusia*, and the industry of producing refined sulphur therefrom is centred in Almeria.

Very large quantities of sulphur are said to exist in *Iceland*, even more important than those in Sicily; the deposits at Guldbringe Syssel, in the south-west of Iceland, were some time ago at work with satisfactory results (Chem. News, xl. p. 31).

Brimstone is got near Mossul in *Mesopotamia*, near *Cairo*, and in *Tunis*. At Djemsah and Ranga, on the coast of the *Red Sea*, the "Compagnie Soufrière" is said to get 300 tons monthly.

Japan possesses very large stores of brimstone, but the absence of facilities for increasing the output of sulphur and for shipping it has hitherto very much restricted the development of the sulphur industry in that country. At present (comp. J. Soc. Chem. Ind. 1890, p. 334) there is only one place where sulphur is worked on any scale, namely Atosanobori, near Kushiro, on the south-east coast of the island in which the port of Hakodate is situated. The Atosanobori mine is part of an extinct volcano, whose crater and slopes are partially covered with a 50-per-cent. sulphur-ore. According to the lowest estimate there is a million tons of good ore there, but probably there is five times as much. The output is at present about 9000 tons per annum; the cost of the sulphur free on board at Kushiro is about 30s. 10d., but it has hitherto been shipped from Hakodate, where it costs £2 3s. 2d.

per ton, which is not remunerative. The exportation was 1541 tons in 1885, 4972 tons in 1886, 7096 tons in 1887, 3609 tons in 1888. The shipments generally go to San Francisco.

Apart from the ordinary yellow sulphur, which sometimes contains traces of selenium and tellurium, there occurs in Japan an orange-red variety, containing 0·17 per cent. Te, 0·06 Se, 0·01 As, traces of molybdenum and earthy matters (Divers and Shimidzu, Chem. News, 1883, No. 1256).

A small island belonging to New Zealand, evidently the crater of a huge submerged volcano, which contains large deposits of sulphur, has been described by MacIvor (Chem. News, 1887, lvi. p. 251). It will probably be very soon submerged as well.

In the *United States of America* brimstone has been found in many places, particularly at Cove Creek, Millard County, South Utah; at Rabbit-Hole springs, Humboldt County, Nevada; near Lake Charles, Louisiana; in Wyoming and other Rocky Mountain Territories; in Texas, California, and so forth. Very few of these occurrences are worked, either owing to the smallness of the stock or to the difficulties of carriage. The Rabbit-Hole mines have been worked off and on, but never at a considerable rate. For the purpose of working the best deposit, the Cove Creek mine, a Company (the Dickert and Myers Sulphur Company) was formed with a capital of \$2,000,000, which acquired Dickert's patents, mentioned on p. 16; but it did not produce more than about 2000 tons of brimstone in 1886, and 2700 tons in 1887, so that it could not even supply all the needs of the Pacific coast, which amount to 4500 tons, and have to be made up from Sicily and Japan (details in the 'Mineral Resources of the United States,' Calendar years 1885, 1886, and 1887).

According to the same official source, the quantity of sulphur imported and entered for consumption in the United States during the years 1877 to 1887 was as follows (most of the crude sulphur coming from Italy), expressed in long tons:—

Fiscal years ending June 30.	Crude. tons.	Flowers. tons.	Refined. tons.
1877	42,962	116	1170
1878	48,102	158	149
1879	70,370	137	68

Fiscal years ending June 30.	Crude. tons.	Flowers. tons.	Refined. tons.
1880	87,837	123	158
1881	105,096	97	70
1882	97,504	158	58
1883	94,539	79	115
1884	105,112	178	126
1885	96,839	220	114
1886	117,538	212	116
1887	96,881	278	83

America furnishes brimstone also in many other places, as in the volcanic regions of Ecuador and Mexico, at Chillan in Chili, and elsewhere.

It has long been known that the crater of the Popocatepetl, in Mexico, contains large quantities of brimstone; and a railway has been projected in order to get at it. An annual production of 50,000 tons of brimstone was expected to begin with, and vitriol-works were to be erected all along the line (Fischer's Jahresh. 1884, p. 265). So far this project does not seem to have been carried out.

On the island of Saba, one of the Antilles, there is a bed of brimstone, yielding on an average 45 per cent. of sulphur, which was worked for some time, but had to be given up again as not paying the expense (Dingl. Journ. 1886, cclix. p. 43).

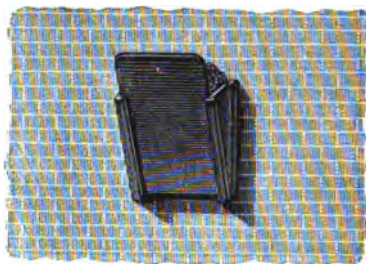
Sulphur Manufactured from other Materials.

Free sulphur is produced in large quantities in the manufacture of coal-gas, and is contained in the *spent oxide of iron*. We shall treat of this later on, as material for producing sulphur dioxide; in this place we mention it only as a source of obtaining free sulphur. This is sometimes done by extracting it with carbon disulphide; but this process does not generally seem to pay (comp. J. Soc. Chem. Ind. 1883, p. 491). Some of the processes described below are specially intended for this kind of material.

A certain quantity of sulphur is obtained by the *distillation of pyrites*. This, however, pays in very few places, except under special circumstances—for instance, at the works of T. D. Starck in Bohemia, which supply nearly all the fuming oil of vitriol, and where the distillation of pyrites is practised in order to obtain a

material for copperas-making. Between 1863 and 1872, 2440 tons of sulphur were thus made. The distillation takes place in earthenware tubes 3 ft. 3 in. long, 5 in. high, and $5\frac{1}{2}$ in. wide, quite open at the back, and in front narrowed to an opening of $\frac{3}{4}$ in. diameter; they are glazed with common salt; and three tiers of seven tubes each are placed in each furnace. For each tube there is a small receiver of sheet-iron half filled with water, and attached to the tapering end of the tube. The charge of pyrites is put into the open end; a slanting piece of sheet-iron is placed in front; and the opening is closed with sand or pyrites cinders, as shown in fig. 1.

Fig. 1.



Here only one third of the sulphur contained in the pyrites is gained; but in Sweden half (?) of the sulphur is said to be obtained in a furnace built similar to a lime-kiln, and continued at the top in a wooden chimney serving as condensing space. The kiln, having been first made red-hot, is charged with pyrites, of which one portion is burned whilst the other portion volatilizes and is condensed at the top. The work is carried on continuously, fresh pyrites being from time to time introduced through an opening near the top, and the cinders being removed at the bottom.

P. W. Hofmann (Dingl. Journ. cxx. p. 232) has made a proposal for utilizing the sulphur of the pyrites smalls, which are obtained in enormous quantities at the pyrites-mines and are very difficult to sell. If sulphurous acid is conducted over red-hot calcium sulphide (from alkali-waste), it is at first completely absorbed; afterwards sulphur distils over, and the calcium sulphide is transformed into sulphate. The latter, by conducting ordinary coal-gas over it in a red-hot state, or by mixing it with coal and igniting, is reconverted into sulphide, which can be used over

again. Hofmann proposes to burn the pyrites smalls at the mines, to obtain their sulphur by means of calcium sulphide in a state fit for sale, to treat the cinders by a process to be described in the 14th Chapter for zinc chloride and sodium sulphate, and to work the residue for pig-iron in a blast-furnace. This proposal has not found any application in practice, and is not likely to do so, since the burning of pyrites dust by the shelf-furnace is equally advantageous for acid-making with that of lump ore.

Gerlach (German Patent 229, 3rd July, 1877) proposes to obtain sulphur from sulphur-ores, and especially from the spent oxides of gas-works, by heating them in iron or fireclay retorts whilst at the same time superheated steam is passed through. The sulphur is said to distil very rapidly. A description of this process, with diagrams, is found in Wagner's *Jahresb.* 1879, p. 268. It was tried in Upper Silesia with sulphur marl, but did not answer (Fischer's *Jahresb.* 1882, p. 234).

O. C. D. Ross has patented a process in every way similar to Gerlach's (E. P. No. 713, of 1879). Other processes of the same kind are described in the '*Scientific American*,' xxxix. p. 276, and in the '*Chemiker-Zeitung*,' 1879, p. 241, by Dubois (E. P. No. 13,108, of 1885, and No. 7129 of 1886; G. P. 41,718: the last patent describes a revolving retort).

According to a French patent of the Société de St. Gobain (No. 107,820, 28th April, 1875), on the top shelf of an ordinary shelf-burner for pyrites smalls (see Chapter IV.) a fireclay retort is to be placed, in which the pyrites is first deprived, by distillation, of a portion of its sulphur, which is collected in the well-known condensing-chambers as flowers of sulphur. After some time the partially desulphurized pyrites is let down to the next lower shelf, and so forth lower down. Here the remainder of the sulphur burns, and the gas goes into acid-chambers, whilst its heat causes the distillation of further portions of pyrites in the retort. This process does not answer: the flowers of sulphur obtained is very acid; and both the burner and the chambers work very badly. A similar process has been again patented by Labois (E. P. No. 9761 of 1884).

Holloway's process (E. P. No. 500 and 1131, 1878) at one time roused much attention. He blows heated air through melted iron sulphide, thus decomposing it into a cupreous matt and a slag, together with free sulphur, which distils off and can be collected.

The principal aim of this process was the concentration of poor copper-ores in countries where fuel is expensive. It has been described by the inventor in a paper read before the Society of Arts, which has been published together with the discussion following the reading of the paper. Bode (Dingl. Journ. ccxxxii. p. 433) has criticised it. Dr. Angus Smith (Alkali Reports, 1877-78, p. 47) expected important results from this process, which is decidedly very interesting; but it has found no practical application.

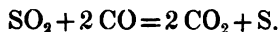
C. F. Claus (E. P. 6909, 1887) treats metallic sulphides with superheated steam, and treats the sulphuretted hydrogen thus evolved with a sufficient quantity of air to produce sulphur.

A. M. and I. F. Chance (E. P. 2495, 1888) reduce calcium sulphate or old (oxidized) alkali-waste by igniting it with carbon, and treat the product, mixed with water, with lime-kiln gases, exactly as will be described in Vol. II. for the recovery of sulphur from alkali-waste. The H_2S evolved is worked either for sulphuric acid or for free sulphur by the Claus process.

Hislop (E. P. 2730, 1882) converts spent gas-lime by heating with tar or coke into a mass containing very much calcium sulphide, which is then decomposed by CO_2 , the H_2S being employed for the recovery of sulphur.

The production of *sulphur from sulphuretted hydrogen*, especially the "Claus" process, will be described in detail in the Chapter treating of the recovery of sulphur from alkali waste. *Alkali-waste* has thereby recently become an important source of sulphur, much more so than it used to be.

It has often been proposed to prepare sulphur by *passing gases containing sulphur dioxide through red-hot coal*. A special apparatus for this purpose has been proposed by Haenisch and Schroeder (E. P. 6404, 1885). They pass the gases first through fire-clay cylinders filled with coke and heated from the outside by producer-gas; the products of combustion travel through another cylinder, filled with open brick-work and heated by the waste fire-gases of the first operation; here the undecomposed SO_2 , the carbon monoxide, carbon disulphide, and carbon oxysulphide act upon one another, so that, if the current has been properly regulated, ultimately only CO_2 and S are formed. Or else the SO_2 is at once treated with CO, according to the equation



This process has been carried out on a large scale at Oberhausen (comp. Chem. Zeit. 1886, p. 1039, abstracted in J. Soc. Chem. Ind. 1886, p. 534).

J. and F. Weeren obtain the SO_2 for this purpose by calcining sulphates with silica (G. P. 38,014). They describe a special apparatus for this reduction and the reduction of the SO_2 by incandescent coke to S.

Technical Analyses of Brimstone.

In trade, three *qualities* of Sicilian brimstone are distinguished. The "firsts" consist of large, shining pieces, of amber-colour, and are rarely used for vitriol-making; the "seconds" are not so shining, but still purely yellow; the "thirds" are of a dirtier colour; and both the latter qualities, as they arrive in England, contain much powder. They are generally very little contaminated with impurities, and often only leave $\frac{1}{2}$ per cent. of ash, very rarely more than 2 per cent.

The ordinary *technical assay* of brimstone is that by burning a weighed quantity, say 10 grams, in a small porcelain capsule, and estimating the quantity of ash left behind. It is, however, advisable to estimate also the moisture, for which purpose, in order to prevent any evaporation during grinding, an average sample of the unground or merely roughly-crushed material, weighing 100 grams, is dried at 100°C . for some hours in an oven or water-bath.

Macagno (Chem. News, xliii. p. 192) has given a process for the direct estimation of the sulphur in crude ores, by dissolving the sample in carbon disulphide and taking the specific gravity of the liquid, from which, by means of a special table, the percentage of sulphur is calculated (comp. also Lunge and Hurter's 'Pocket-Book,' p. 80).

Arsenic sometimes occurs in brimstone, more especially in that recovered from alkali-works, always in the shape of arsenious sulphide. On extracting the brimstone with disulphide of carbon, the As_2S_3 remains behind and can be estimated. Schaeppi (Chem. Ind. 1881, p. 409) prefers extracting the As_2S_3 with dilute ammonia (as described by the German Pharmacopœia) at 70° or 80°C . In the solution the sulphur can be precipitated with silver nitrate as Ag_2S , which is filtered, washed, dissolved in hot nitric acid, and estimated as chloride; 6 molecules of AgCl correspond

to 1 of As_2S_3 . It is, however, more expeditious to work volumetrically. The ammoniacal solution of arsenious sulphide is exactly neutralized with pure nitric acid, strongly diluted and titrated with decinormal argentic nitrate, till a drop of the solution, on addition of neutral potassium chromate, produces a brown colour. When employing 10 grams of sulphur for extraction with ammonia, each c. c. of decinormal silver solution indicates 0.041 per cent. As_2S_3 . Sometimes arsenic occurs in recovered sulphur in the shape of ferric or calcium arsenite which cannot be found by the above process, but only by extracting the sulphur with carbon disulphide and digesting the residue with aqua regia.

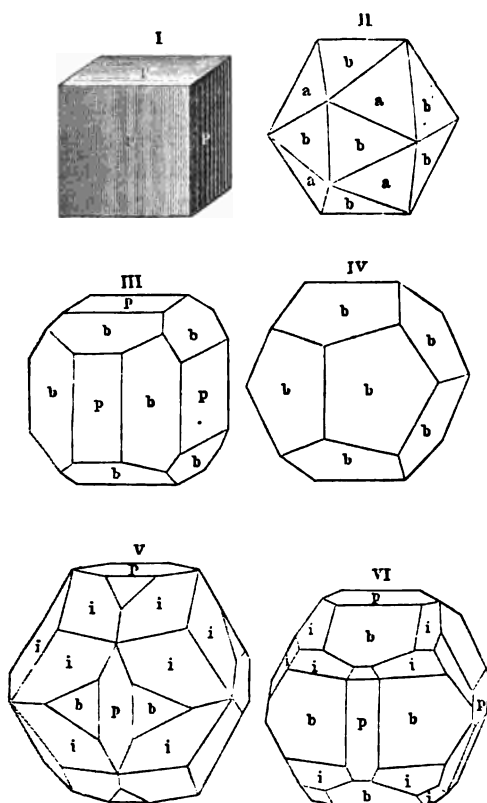
2. PYRITES.

What is called *pyrites* or *iron-pyrites*, in a technical sense, is hardly ever pure iron disulphide, FeS_2 , but either a mixture of this with gangue, or more frequently at the same time with other sulphuretted ores, as shown by numerous analyses. The iron disulphide may be present either as iron-pyrites proper or as marcasite. The iron-pyrites proper crystallizes in the regular system, with parallel hemihedry, proved even on the faces of the cube by striation (fig. 2).

Besides the cube (I), the octahedron, *a* (II), is frequently found, often modified by the pyritohedron, *b* (III), and, if both are equally developed, forming the icosahedron (II). The combined forms IV, V, and VI, as well as twin crystals, frequently occur. The crystals are often well developed; but in the pyrites used on the large scale they are mostly quite indistinct. The colour of pure pyrites is greyish yellow, and easily distinguished from that of copper-pyrites. The microcrystalline pyrites of trade often shows other colours, even a slate-grey; the powder is brownish black. Its cleavage parallel to the faces of the cube is not very pronounced; the fracture is conchoidal or irregular. Hardness 6 to $6\frac{1}{2}$, specific gravity 4.83 to 5.2. Pure FeS_2 contains 46.67 per cent. of iron and 53.33 per cent. of sulphur.

According to Mène, the pyrites from volcanic formations contains no water, but that from sedimentary strata both water and clay. Among the first he classes the yellow octahedral pyrites, which is stable in the air; among the latter the grey cubical pyrites, which is easily transformed into ferric sulphate (Compt. Rend. 29th April, 1867).

Fig. 2



Marcasite crystallizes in the rhombic system, in rhombical prisms $M=106^{\circ} 2'$ with longitudinal faces $l=100^{\circ}$ and r , and the end face P inclined to r at an angle of $158^{\circ} 20'$. They frequently occur in twin crystals, partially united along one of the faces M , also in triplets and quadruplets, &c. (fig. 3), in fibrous, bulbous, &c. varieties; cleavage indistinct; hardness 6 to 6.5; specific gravity 4.65 to 4.88; colour grey to yellow or greenish yellow, lighter than iron-pyrites proper; powder greenish dark grey. Marcasite is most frequently found in bituminous slate and

Fig. 3.



coal, and decays even more quickly than pyrites, with formation of copperas and basic ferric sulphate.

In the ores of commerce there is often present, mixed with FeS_2 , *magnetic pyrites* of the formula Fe_7S_8 , with 60·5 iron and 39·5 sulphur; colour between brass-yellow and copper-red; hardness 3·5 to 4·5; specific gravity 4·4 to 4·7.

The *copper-pyrites* so often mixed with iron-pyrites is distinguished from it by its colour, yellow as brass, sometimes as gold; this colour modifies that of the iron-pyrites according to the degree of admixture. It crystallizes in the tetragonal system, but in the ores which concern us always occurs in a microcrystalline form. Its hardness is 3·5 to 4·0, specific gravity 4·1 to 4·3. Pure copper-pyrites of the formula FeCuS_2 should contain 30·53 per cent. iron, 34·58 per cent. copper, and 34·88 per cent. sulphur; but the ores serving for the manufacture of sulphuric acid rarely contain beyond 4 per cent. of copper.

The first application of pyrites for sulphuric-acid-making is generally ascribed to a Mr. Hill, of Deptford, who in 1818 took out a patent for it. In France, Clément-Desormes seems to have made the first proposals and experiments in that way. His trials did not, however, succeed, because he believed it necessary to increase the combustibility of pyrites by an addition of coal. This is both unnecessary, with properly constructed kilns, and very injurious to the process, from the carbonic acid getting into the chambers. A great difficulty was experienced in lighting the kilns. So long as it was attempted to do this from below, like an ordinary fire, the thing would not work. According to communications from Mr. Todd (Government Inspector of Alkali Works), a workman of his father's in Cornwall, in 1830, accidentally discovered the way of lighting the kilns from the top, such as is practised to this day. Generally, however, the principal merit of introducing pyrites is ascribed to Messrs. Perret and Son, of Chessy, who were led to it by the necessity of desulphurizing their cupreous pyrites previously to getting the copper, and of condensing the gas evolved. There was no question then of supplanting the Sicilian sulphur generally. Perret and Son, with the greatest care, searched into all the conditions necessary for a proper combustion of the ore; and to them the honour is due of having overcome all the difficulties opposed to the solution of this problem, and of having rendered the process technically useful. Already in 1833 they had burnt iron-pyrites

successfully; and in a patent dated November 20th, 1835, they described their process, to which their partner, Olivier, is said to have given the first impulse. In 1837, Messrs. Wehrle and Braun, in Bohemia, used pyrites for generating sulphurous acid (Otto, 'Lehrbuch der Chemie,' 4th ed. iii. 1, p. 545); but, according to Bauer (*l. c.* p. 6), I. Brem had introduced this process into Austria already in 1833—that is, at the same time as Perret.

These trials at making vitriol from pyrites possessed, however, only local interest; and probably for a long time no general attempt to do away with Sicilian brimstone would have been made, but for the Neapolitan Government, in 1838, being induced to grant a monopoly for the exportation of Sicilian sulphur to the Marseilles firm of Taix and Co. This firm at once raised the price of brimstone from £5 to £14 per ton, and thus would have given a fatal blow to the manufacture of artificial soda-ash, just then beginning to take a firm hold, if no other source of sulphur had been known in the world, and if such an unnatural measure could have been carried out at all. But the attempt came too late—just after Perret and Son had proved that the pyrites occurring in most industrial countries could be used for vitriol-making without any difficulty. The result was to be foreseen. Once the discovery of a new source of sulphur had become a matter of necessity, there were, within twelve months from the rise in the price of brimstone, fifteen patents taken out in England for burning pyrites for the purpose of making sulphurous acid, and even a larger number for making sulphur from pyrites, gypsum, &c.

According to Muspratt's 'Chemistry' (vol. ii. p. 1023), Dr. Thomas Thomson was the first in England to point to pyrites in this crisis; but most probably many others at the same time turned to it. So much is proved—that Thomas Farmer, of London, was the first in England who employed pyrites on a large scale (in 1839) for the manufacture of sulphuric acid (Hofmann, 'Report by the Juries, International Exhibition, 1862, Class II. Section A,' p. 12).

Mr. E. K. Muspratt states that his father, in 1839 and 1840, used large quantities of Wicklow and Welsh pyrites at Liverpool and Newton, the cupreous cinders being sent to the Sutton Copper Company at St. Helens.

In Germany the Oker works, at the Rammelsberg, near Goslar, seem to have been the first who calcined the local ore in such a

way as to convert the sulphurous acid given off into sulphuric acid in acid-chambers (in 1840); and other smelting-works, such as those at Freiberg, followed their example. In these cases the reasons were, not only that at a comparatively small expense sulphuric acid could be obtained as a by-product from the sulphurous acid otherwise lost, but also that the acid fumes destroyed the vegetation of a large district round the works, and that means had to be taken for preventing this, apart from any consideration of profit.

The Sicilian-brimstone monopoly certainly did not last long; diplomatic pressure on the part of England soon led to its abolition; and with the lowering of the price of brimstone most works at first returned to its employment. But the ice was now broken; the conviction had been gained that it was possible to make acid without Sicilian brimstone; the owners of pyrites-mines took pains to advance the use of pyrites by low prices; and thus, in the course of the next twenty years, gradually, but steadily, brimstone was more and more driven from its place in sulphuric-acid-making, in proportion as, on the one hand, it became dearer from the causes above mentioned (disease of the vines &c.), and as more pyrites-mines were opened out. In 1852 brimstone was no longer used in Lancashire, but on the Tyne 7580 tons of it were still burned.

The decisive point in favour of the use of pyrites was this, that more and more *cupreous pyrites* came into the market, from Spain especially (first in 1859), but also from other countries. These had at any rate to be burnt and their sulphur expelled before they could be worked for copper. Already with Perret and Son this had been the stimulus for their efforts; but this has been done on a much more colossal scale in consequence of the opening out of the cupreous-pyrites mines in the south of Spain, in Portugal, and in Norway. In England, now-a-days, iron-pyrites is all but out of the field, and has been supplanted by cupreous pyrites. This has been the case to a smaller extent in France and Germany up to the last few years, because these countries possess sufficient mines of rich pyrites, which in England are not numerous; but even in those countries more and more cupreous pyrites is coming into use. In 1867 pyrites had almost entirely supplanted brimstone in France as a raw material for acid-making in the large industrial centres ('Rapport du Jury International, Expos. Univ. de 1867,' vol. vii. p. 19). In Germany this state was brought about somewhat later, but

quite as completely. Only during the feverish years 1871 to 1873, when the price of pyrites had risen very high, a few factories in Hanover, in Hamburg, and Stettin temporarily returned to the use of brimstone (Hasenclever, *l. c.* p. 155); but with lower prices of pyrites this has been given up again.

Thus, starting from the use of iron-pyrites, that of cupreous pyrites has followed; and to this was added the employment of other sulphurous ores, and of the intermediate products of smelting—for instance, copper-regulus (“coarse metal”) at Mansfield and Swansea. At the present time the Freiberg works work even poor lead-matts with about 22 per cent. of sulphur, which a few years ago was thought impossible (Bode, ‘*Beiträge zur Theorie und Praxis der Schwefelsäurefabrikation*,’ 1872, p. 1). We shall further on describe the application of other sulphur-ores apart from pyrites proper.

An idea of the extension which the use of pyrites has obtained is given by the subjoined Table of the importation of pyrites into Great Britain (p. 32).

The *principal sources of pyrites* will now be mentioned without separating the cupreous from the non-cupreous, because no strict limit can be drawn. Some kinds of pyrites contain so little copper (below 1 per cent.) that it cannot be utilized; and these go with the totally non-cupreous ores.

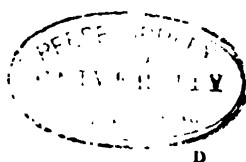
Great Britain possesses several deposits of pyrites, but none of very great importance. In Cornwall and Devonshire pyrites of the following composition is found:—

	Pattinson.	Clapham (8 analyses).
Sulphur	27·00	24·013–34·880
Iron	22·69	27·076–60·676
Copper	2·00	0·400– 4·600
Lead	trace	0· – 7·446
Zinc	1·23	0· – 9·086
Lime	0·22	Gypsum 0· – 0·596
Carbonate of Lime	0· – 3·579
Magnesia	0·12	
Arsenic	0·32	0· – 1·160
Insoluble (silica)...	45·60	2·000–38·676
Oxygen as Fe_2O_3 ...	0·13	
Moisture	0·64	
	<hr/> 99·95	

Cleveland pyrites (from the north of Yorkshire) is only used in a local factory; in 1874, 500 tons of it were obtained. Composition (according to Pattinson's analysis):—

Iron disulphide.....	52·12
(corresponding to 27·18 sulphur).	
Iron protoxide	11·92
Alumina	8·10
Lime	0·27
Magnesia	1·00
Carbonic acid	2·40
Insoluble in acid	11·12
Water	12·86
	<hr/>
	99·79

In *Ireland* there are large beds of pyrites, especially in the county of Wicklow; and up to about 1862 this Irish ore supplied a very large portion of the pyrites used in England. In 1860 still 40,000 tons of it were imported into the Tyne river; but in 1863 the importation had fallen to 4000 tons, and has long since ceased entirely. The same has been the case in Lancashire; and only a few works in Ireland itself burn this kind of pyrites. It is found in the county of Wicklow in beds from 6 to 50 feet in thickness, which overlie siliceous clay-slate. The beds go down to depths of 80 to 100 fathoms. The bulk of the ore contains only 30 to 35 per cent. of sulphur. A small quantity only of richer ore (analyses *a*, *b*, *c*) has been found in the valley of Ovoca. The Irish ore is too hard and slaty, and does not burn well; it requires a great heat, and consequently deep kilns. It nearly always contains copper, but rarely sufficient to pay for extracting it, from which standpoint the following analyses must be judged. Its production (formerly much more considerable) had in 1874 fallen to 18,272 tons.



	Pattinson.	Clapham.			
	a.	b.	c.	d.	e.
Sulphur	44.20	40.410	42.128	37.975	34.676
Iron	40.52	32.222	35.000	34.650	42.400
Copper	0.90	4.133	2.400	2.400	1.333
Lead	1.50	2.963	1.600	1.080	1.593
Zinc	3.51
Arsenic	0.33	...	0.602	0.400	0.183
Lime	0.24
Insoluble	8.80	17.676	18.676	22.500	20.000
Moisture.....	0.09
Oxygen as Fe ₂ O ₃ ...	0.25
	100.34	97.404	100.406	99.005	100.185

In *Wales* (in the Cae Coch Mine) pyrites is found, entirely free from arsenic, according to Drinkwater (*Journ. Soc. Chem. Ind.* 1885, p. 533). It contains 48.3 per cent. of sulphur, and is used for manufacturing very pure oil of vitriol.

According to Hunt's Mineral Statistics for 1882, p. 85, there was produced in the United Kingdom :—

Iron Pyrites from Mines under the Metalliferous Mines
Regulation Acts.

	tons.
In Anglesea	110
„ Carnarvonshire	5889
„ Cornwall	764
„ Devonshire	717
„ Leinster.....	11,074
Total.....	18,554

Iron Pyrites and Copperas Lumps from Mines under the Coal
Mines Regulation Acts.

In England.....	6626
„ Scotland	221
	6847

In 1886 the total production of iron-pyrites in the United Kingdom amounted to 27,829 tons, in 1887 to 22,079 tons.

A certain quantity of pyrites is picked from coals, and is known as *coal-brasses*. If quite free from coal, they are very rich—according to R. D. Thompson (in Richardson & Watts's 'Chemical Technology,' vol. i. pt. iii. p. 15), 53.55 sulphur, 45.07 iron, 0.70 manganese, 0.80 silica; but practically they cannot be obtained in this state, and the

carbonaceous matter adhering to them causes very much trouble in the vitriol chambers. Their only legitimate use in acid-making is for lighting the burners, or at most for getting up their heat if it has gone down. Apart from this they are worked up by weathering for copperas and Venetian red, and this is probably the way in which most of the quantity obtained in England (10,000 tons in 1874) is consumed.

The most important *German* pyrites-bed is that of *Meggen* in the Siegen district, in Westphalia, 3 miles from the Altenhunden station on the Ruhr-Sieg railway. This bed occurs along with heavy spar in the so-called "Kramenzel;" it is known for a length of 2000 fathoms; and its thickness changes from $\frac{3}{4}$ to 3 fathoms (Wagner's 'Jahresbericht,' 1865, p. 221). The same authority states it to be "grey iron-pyrites," quite uncrystalline, free from arsenic [?], of equal composition throughout, and containing 47·50 sulphur, 43·55 iron, 0·32 carbon, 8·22 silica; but this analysis is far too favourable if referred to the bulk of the ore. The mass of ore above the bottom of the valley is estimated at $4\frac{1}{2}$ million tons; how far the ore may go down below the bottom of the valley is as yet unknown. The quantity got yearly is stated in the table at p. 37.

The ore has not an attractive outward appearance; its colour is slate-grey; but it burns very well in the kilns, and it would be even more valuable if the zinc contained in it did not prevent its burning completely. Fresenius analyzed a large average sample of this Meggen ore from the "Sicilia" pit, and found 45·42 per cent. of sulphur and only 0·02 per cent. of arsenic; this agrees with Pattinson's analysis of the average sample of a whole cargo (in his paper read to the British Association at Newcastle-on-Tyne in 1864), which shows:—

	per cent.
Sulphur	45·60
Iron	38·52
Lead	0·64
Thallium	trace
Zinc	6·00
Cobalt	trace
Arsenic	trace
Lime	0·11
Insoluble, silica &c.	8·70
Oxygen (as Fe_2O_3)	0·37
Moisture	0·36
	<hr/>
	100·30

Hjelt (Dingl. Journ. ccxxvi. p. 175) found 0·30 per cent. As. Latterly the pyrites obtained is rather poorer, and its average percentage of sulphur only amounts to 41 or 42 per cent. Owing to the competition of cupreous pyrites, its exportation to other countries has very much decreased of late; and in Germany itself it has lost much of its importance.

There are smaller beds of pyrites in several other places in Germany, such as those near Goslar, near Schwelm in Westphalia, near Merzdorf in Silesia, &c. Their production is only small compared with that of the Meggen pyrites. The pyrites of the Rammelsberg in the Harz, according to Mène, contains 48·4 per cent. of sulphur (probably only picked lumps). The cupreous pyrites of the same place is stated by Hilgenfeld to contain:—

Copper	12·22
Lead	2·43
Iron	39·10
Zinc, Manganese, Cobalt, Nickel	1·23
Arsenic	0·18
Antimony	0·16
Sulphur.....	44·65
Selenium, Thallium, Indium, Bismuth	traces
	<hr/>
	99·97

The bed of *Schwelm* in Westphalia, in the Devonian formation, has a thickness of from 10 to 33 feet, over a surface of nearly 150 acres, and is covered by rich iron-ore; the pyrites itself consists of two thirds powder mixed with well-crystallized pieces. The ore contains about 40 per cent. of sulphur, and more or less clay, which is removed by washing; after this it is sold to the vitriol-makers, who like it on account of its freedom from arsenic (Dingl. Journ. ccxxviii. p. 283); Hjelt, however, found more arsenic in it than in Meggen pyrites.

On the Island of Wollin a pyrites-bed is found in a bed of marl belonging to the chalk formation.

A great drawback to the German ores is their proportion of zinc, which retains a considerable quantity of sulphur in the state of sulphate. In Silesia 14 per cent. of zinc is allowed as a maximum; upwards of this for each per cent. of zinc the same quantity

of sulphur is deducted from the invoice (Kosmann, in Fischer's Jahresb. 1886, p. 268).

The production of pyrites in Germany has been as follows :—

Year.	Meggen mine.	Schwelm mine.	Total in Germany.
	tons.	tons.	tons.
1853	594	147	
1855	1906	330	
1860	9892	26888
1865	33993	326	40226
1870	92048	700	102742
1871	110432	1383	122401
1872	143476	1840	152916
1873	123002	8285	131712
1874	120209	7300	131619
1875	110587	8785	126443
1876	88186	13249	113703
1877	61197	25579	107681
1878	59920	26495	101089
1879	60241	28460	100509
1880	62301	37700	112288
1881	76418	34915	125057
1882	111159	29790	158418
1883	109863	26890	149520
1884	109585	30325	150130
1885	84970	18726	116212
1886	81285	14400	113655

In *Belgium* there is a rich pyrites, the great friability and softness of which do not tell in its favour. The following are analyses of this pyrites :—

	a.	b.	c.	d.	e.	f.
Sulphur	42.80	35.50	46.20	45.01	50.00	45.60
Iron	36.70	38.60	40.50	39.68	43.61	38.52
Ferric oxide	7.23	4.24	2.20			
Oxygen in ferric oxide }	0.32	0.18	6.00
Lead	0.92	0.65	0.41	0.37		
Zinc	0.40	5.26	0.22	1.80	1.75	
Arsenic	0.20	0.31	0.41	trace	trace	trace
Thallium	trace		
Alumina	trace					
Silica	8.86	14.90	9.10	12.23	2.85	9.00
Carbonic acid	0.73	
Calcium carbonate	0.84	trace	0.11
Lime	0.25	0.92	
Water	1.46	0.56	0.42	0.25	0.10	0.36
	99.41	100.02	99.46	99.91	100.14	99.59

(*a*, *b*, and *c* by Clapham in Richardson and Watts's 'Chemical Technology,' vol. i. part iii. p. 14; *d*, pyrites from Rodieux near Spa, *e*, from Santon's pit on the Meuse, both by Pattinson, *l. c.*; *f* by MacCulloch, Chem. News, xxvii. p. 125.)

The Belgian pyrites is usually only got as a by-product in the getting of lead- and zinc-ores in the provinces of Liège and Namur; it is either microcrystalline or crystalline or in bulbous pieces with a concentrically fibrous structure. Its quality is uneven. It is mostly used locally and in the north of France; the export to England seems to have ceased.

The production of pyrites in Belgium has been as follows:—

Year.	tons.	Year.	tons.
1840.....	500	1875.....	30,747
1850.....	4,084	1879.....	15,577
1860.....	42,513	1880.....	7,913
1865.....	31,818	1881.....	2,965
1870.....	28,665	1882.....	2,555

In *Hungary* very good pyrites occurs at Schwellnitz, containing 46 or 47 per cent. of sulphur and a few per cent. of copper. It is heavy, but very porous, and burns very well; but it is rather explosive. This ore is used at the Aussig works.

In *Styria* (Riedl, Zeitschr. f. d. chem. Grossgewerbe, ii. p. 567), in the Saun valley, a number of beds of very pure but easily decomposable pyrites occur in the clay porphyry, with a percentage of 48 to 52 of sulphur. It is used in the chemical works at Hrastnigg and in Bohemia. The production is about 3000 tons per annum (Fischer, Jahresb. 1886, p. 255).

In *Switzerland*, in the Canton of Wallis, a pyrites occurs which does not seem to have found any technical application as yet. Its composition, according to an analysis made in my laboratory, is:—

Sulphur	50.46	(of this 0.05 as lead
Iron	44.55	sulphate in the in-
Lead	0.37	soluble residue).
Lime	1.13	
Magnesia	0.11	
Carbonic acid	1.01	
Silica, Iron peroxide, } Alumina..... }	1.70	(insoluble)
Moisture.....	0.40	

In *France* the principal deposits of pyrites are those of the Rhone (Chessy and Sain-Bel) and of the South (Gard and Ardèche). The Rhone beds exist on both banks of the Brevenne, a tributary of the Saone, on a width of 4 or 5 miles. The bed on the left bank is that of Chessy, about 6 miles long and several yards thick. This pyrites is bright yellow, very crystalline and friable. When first got it contained 4 or 5 per cent. of copper; but the cupreous vein has run out, and the non-cupreous ore on this side has nearly ceased to be worked. The beds on the right bank are those of Sain-Bel or Sourcieux. The northern part furnishes a more compact ore than the Chessy ore. Most of it is non-cupreous, but there is also a vein with 4 or 5 per cent. copper; the gangue is mostly sulphate of baryta. Much more important is the southern part of this bed, the "*masse de Bibost*." The ore is here very rich in sulphur, green with yellow reflexion, and very friable, so that there is almost as much smalls as lumps; the gangue is almost entirely siliceous. The beds in the South of France are more numerous, but much less important. The most considerable mine is that of Saint-Julien-de-Valgalgues, in the Département du Gard; there is another mine at Soyons, in the Ardèche. The other French mines are of little importance. A detailed description of the French pyrites-mines has been made by Girard and Morin (*Compt. Rend.* 1875, lxxxi. p. 190; *Annales de Chimie et de Physique* [5], vii. p. 229); from this paper the following analyses are extracted, which seem more trustworthy than those by Mène, given in the 1st edition of this book, p. 92, from the *Monit. Scient.* 1867, p. 410).

These analyses may be summed up as follows:—The pyrites from the Rhone and Sain-Bel, on an average, contains 46 to 48 per cent. of sulphur and 10 to 12 per cent. of gangue, consisting of clay, sand, and barytes. In the southern part of the district of Sain-Bel the percentage of sulphur rises to 50 or 53, and the gangue is inconsiderable and free from barytes; arsenic is not present in quantities sufficient for determination. In the district of St. Julien (Le Gard) pyrites is not found in the clay-slate, as at Sain-Bel, but in the Lias or Trias; the sulphur varies from 40 to 45 per cent.; the gangue is calcareous, and varies from 3 to 6 per cent.; arsenic is present up to 0.1 per cent., sometimes also fluor spar in quantities sufficient for estimation. The pyrites from Ardèche contains from 45 to 50 per cent. of sulphur; the

	Cheesy.		Sain. Bel.			Masse de Bibost.	
	Lumps.	Smalls.	Non-cupreous.	Cupreous.	55 metres underground.		115 m. underground.
					I.	II.	
Sulphur	47.34	48.57	46.62	37.89	47.1	47.98	52.49
Iron	41.72	43.20	39.07	29.92	40.5	41.11	46.43
Copper	0.05	trace	...	4.61
Zinc.....	6.86
Arsenic	0.02	trace	0.05	0.06	trace	trace	slight trace
Gangue	10.79	4.71	13.92	21.25	12.4	10.78	0.90
Moisture	0.08	3.52	0.17	0.09	...	0.20	0.04

	Saint-Julien.				Soyons.
	Outcrop (picked).	32 metres underground.	50 metres.	87 metres.	
Sulphur.....	49.11	44.13	42.87	41.13	43.94-49.68
Iron	43.24	38.24	37.94	36.85	39.15-43.04
Arsenic	0.11	0.05	0.10	0.08	0.16- 0.39
Calcium carbonate	2.56	5.52	2.86	9.69	...
Magnesium carbonate.....	trace	trace	trace	0.08	...
Calcium sulphate.....	0- 1.67
Calcium fluoride	1.09	trace	trace	trace	trace- 0.63
Insoluble	2.48	10.20	13.19	11.23	4.15-11.76
Oxygen in excess	1.40	0.88	0- 1.02
Moisture	1.33	1.74	1.59	0.57	0.86- 4.58

gangue is clay, free from lime; arsenic occurs up to 0·3 per cent.; fluor spar sometimes occurs in injurious quantities: the hydro-fluoric acid given off from it in one case destroyed the glass apparatus for spreading the nitric acid; and the latter thus got to the chamber-bottom and corroded it.

In 1874 there were used in France 178,400 tons, of the value of £240,000. Of this the beds of Sain-Bel, which supply two thirds of the French factories, supplied 120,000 tons, those of St. Julien (in the department Gard) 24,600 tons, those of Le Soulier (Gard) 6000 tons, those of Soyons (Ardèche) 900 tons. From Belgium, Norway, and Spain 18,000 tons were introduced. Girard and Morin give twenty-three analyses of French and five of foreign pyrites used in France.

According to Scheurer-Kestner (Wurst, Dict. de Chimie, ii. p. 138) the pyrites from Chessy and Sain-Bel contains 45 to 48 per cent. of sulphur with very little arsenic and selenium, that from Chessy also 1 or 2 per cent. of copper and zinc; the copper is obtained from the cinders, at least at the Chessy works themselves, by allowing them to lie for a time and moistening them: the liquid running off contains copper and zinc sulphates; and the copper is got from it by cementation. Nearly all French works, as well as those in Alsace and Switzerland, get their ore from those two pits; only those of the Gard and of Marseilles get it from Alais, where the pyrites contains 38 to 42 per cent. of sulphur: a few factories in the north of France use Belgian pyrites; those in the South use Spanish pyrites.

France imported in 1886	1887
22,172	24,321
and exported 23,518	19,615

tons of pyrites.

Italy possesses beds of pyrites in several places. Those occurring in the province of Bergamo, tested in Vienna (Wagner's Jahresb. 1879, p. 272), are composed as follows:—

	Redolta quarry.	Passavra quarry.	S. Guiseppe pit.	Vallantica pit.
Iron.....	36.29	41.72	48.35	36.79
Copper	trace	trace	0.07	1.69
Zinc.....	trace	...	0.18	...
Lead	trace
Silver	0.014
Sulphur	39.32	44.36	30.97	41.56
Arsenic	0.53	0.14	...	0.18
Alumina	2.37	1.28	1.86	1.25
Lime	5.89	0.88	1.70	0.37
Magnesia.....	0.66	0.39	0.14	0.10
Silica	7.16	9.48	10.45	16.40
CO ₂ , O and H ₂ O (by diff.)	7.78	1.55	6.28	1.646
	100.00	100.00	100.00	100.00

In the Val d'Aosta there are several mines, some of them containing a strongly arsenical pyrites.

Those at Brosso, near Ivrea, belonging to Messrs. Sclopis & Co., yield pyrites containing very little arsenic: present output about 20,000 tons per annum. One quality contains 48 or 49 per cent. of sulphur and 0.2 of arsenic, the other nearly 50 of sulphur and only traces of arsenic. It is too explosive for burning in lumps, but excellent for burning as smalls.

Swedish pyrites, from Fahlun, varies between 43 and 48 per cent. of sulphur. It has only been imported into England in small quantities. This ore is obtained as a by-product in the getting of copper-ores, and is said to exist in enormous quantity; but, owing to the difficulty of transit, its exportation does not pay. It is said to burn well.

	Pattinson.	Browell and Marreco.
Sulphur	43.70	38.05
Iron	39.01	42.80
Copper	0.60	1.50
Lead	0.12	
Zinc	2.57	
Lime	0.85	
Magnesia	0.69	
Arsenic	trace	
Insoluble	11.66	12.16
Oxygen, as Fe ₂ O ₃	0.22	Oxygen } 5.49 and loss }
Water.....	0.20	
	<hr/> 99.62	<hr/> 100.00

In *Norway* there exist very large beds of pyrites, both free from and containing copper. Of the many pits formerly worked there, all those had to stop which produce ores with from 35 to 40 per cent. of sulphur. The richer ores, even those free from copper, have maintained their position to some extent, because they burn well, are easily lighted, keep the heat well, do not "scar," &c. They are mostly hard and difficult to break. The most considerable pits are those of Ytteröen, which export *via* Drontheim; they supply 6000 to 8000 tons per annum. A large mass of cupreous pyrites, with 45 per cent. of sulphur and 3 of copper, exists at Vigsnaes, and is (or was) worked by an Antwerp Company. Norwegian pyrites contains very little arsenic. Other pits exist thirty miles from Drontheim, on the Hardanger Fjord, near Bergen, &c. The Norwegian pyrites is more in favour as a sulphur-ore (excepting its difficult breakage) than as a copper-ore; its cinders do not very well suit the copper-works.

Analyses of Norwegian Pyrites.

	Pattinson.		MacCulloch.	
	Ytteröen ore.	Drontheim ore.	I.	II.
Sulphur	44.50	50.60	46.15	38.17
Iron	39.22	44.62	44.20	32.80
Copper	1.80	trace	1.20	1.10
Zinc.....	1.18	1.34	2.10	2.32
Lead	trace
Lime	2.10	trace
Calcium carbonate.....	2.55	11.90
Magnesia.....	0.01	trace
Magnesium carbonate	1.08
Carbonic acid.....	1.65
Arsenic	trace
Insoluble	9.08	3.15	3.20	12.20
Oxygen, as Fe_2O_3	0.45
Moisture.....	0.17	0.20	0.40	0.25
	<hr/> 100.16	<hr/> 99.91	<hr/> 99.80	<hr/> 99.82

Spain and Portugal possess the largest known beds of pyrites. It is cupreous, and distinguished by its very good behaviour in burners; so that the burners have been built very much lower for it, and much labour is saved. This pyrites has only been worked again since 1855; but the Romans, and before them the Phœnicians and Carthaginians, knew it very well, as is shown by many

traces. The bed, however, was at that time only worked where it was richest in copper. According to Schönichen (Dingl. Journ. clxx. p. 448) all the beds are within a belt of five leagues width, reaching, parallel to the Sierra Morena, from the western frontier of the province of Seville, across the hilly country situated to the south of this, right through Portugal to the Atlantic Ocean—a length of 30 leagues. The prevailing rocks in that country are clay-slate and crystalline slates; but parallel to the granitic tract of the Sierra Morena felsite-porphry and quartzite have broken through the slate, and only in the neighbourhood of such dykes are the pyrites-beds found. Their shape is that of large lenticular pockets in the metamorphic clay-slate, from 20 to 36 fathoms thick, and extending to a length of 170 to 260 fathoms. The whole bed is filled with pure pyrites, without any visible gangue. The ore is in a few places found already at 1 or 2 fathoms below the surface, undecomposed, and in a sandy state; so that it can be got by daylight work. In other places the zone of decomposition reaches from 10 to 50 fathoms downwards. The percentage of copper varies from $2\frac{1}{2}$ to 40; but ores with more than 10 per cent. of copper are only contained in small vertical zones within the large masses. Only these “black” ores were the object of the mining operations on the part of the Phœnicians and Romans. The quantity of pyrites existing there is almost inexhaustible, and can certainly supply the requirements of mankind, both of copper and of sulphur, for thousands of years to come.

Special highways, and latterly also railways, have been made, in order to facilitate the communication with the ports of Huelva, San Lucar du Guadiana, and Pomaron; but a great deal of the ore is still conveyed for some distance on mule-back.

Of the many companies which had been formed for working this ore most have ceased to exist; and only four or five of them have remained, all of them in English hands. The smallest of these is the Buitron Pyrites Company, which works the mines of Buitron and Poderosa. The Tharsis Sulphur and Copper Company possesses much more extensive mines, a railway of its own, a wharf at Huelva, and also a number of works in England and Scotland for the wet extraction of the copper from the cinders returned to them. The Tharsis ore is very good, but very soft, and makes much dust in breaking. The San-Domingo mine lies in Portuguese territory; its ore is known as Mason’s ore, and is considered superior to all others, so that it commands a better price

The last, but largest, of these companies is the Rio-Tinto Company, which has thrown such large masses of pyrites into the English market that, from 1875 to 1876, prices receded by more than one third. Its ore is also of excellent quality. The mines of Carpio and Lagunazo, in the province of Huelva, are not yet worked for exportation.

The Spanish (and Portuguese) pyrites contains never less than 46, and up to 50 per cent. of sulphur, besides 3 to $4\frac{1}{2}$ per cent. of copper, which, however, by most of the English buyers, is not bought, but returned in kind to the seller in the shape of cinders from the pyrites-burners. The value of the copper (if bought) is still fixed by the so-called "Cornish assay"—that is, a process of dry assaying only known to a few assayers living at Redruth and other places in Cornwall, the great inaccuracy of which is perfectly well known to all parties concerned; it shows, for instance, only 2 per cent. if 4 per cent. is actually present; and from this difference the buyer must pay the cost of extracting the copper and his own profit, since the price to be paid for the copper *in the ore* by Cornish assay is sometimes higher than the value of a similar quantity of copper *metal*. This remarkably irrational system has not hitherto been done away with for sales.

In Germany also a few years ago a number of manufacturers united in working Spanish pyrites (especially Rio-Tinto ore), and in delivering all their cinders to the Duisburg copper-works. The Oker works also use similar ores, which they work up themselves for copper.

The ore of the three principal companies is very similar in composition; its analysis is as follows:—

	Pattinson.				Claudet (San Domingo ore).	MacCulloch (San Domingo ore).
Sulphur	48.00	49.60	44.60	49.30	49.00	49.80
Iron	40.74	42.88	38.70	41.41	43.55	42.88
Copper	3.42	2.26	3.80	5.81	3.20	2.26
Lead	0.82	0.52	0.58	0.66	0.93
Zinc	trace	0.10	0.30	trace	0.35	0.10
Lime	0.21	0.18	0.14	0.14	0.10	0.18
Magnesia	0.08	trace	trace	trace
Thallium	trace	trace	trace	trace
Arsenic	0.21	0.28	0.26	0.31	0.47	0.28
Insoluble	5.67	2.94	11.10	2.00	0.63	2.94
Oxygen (as Fe_2O_3) ..	0.09	0.15	0.23	0.25	1.07
Moisture	0.91	0.95	0.17	0.05	0.70	0.95
	100.15	99.86	99.88	99.93	100.00	99.39

Some descriptions of Spanish pyrites are in bad repute with the manufacturers as "explosive" or "detonating," because they decrepitate in the kilns shortly after lighting with loud detonations, and thereby make so much fine powder that the burners are stopped up and "scars" are formed. The reason of this detonating property is probably to be sought in the presence of hydrated silicates (zeolites) in the ore*.

According to Hjelt the average percentage of As in Spanish ores is 0·91.

In 1880, according to Wimmer (Fischer's Jahresb. 1883, p. 257), the total production of pyrites in the South of Spain and Portugal was as follow :—

Rio Tinto	1,000,000 tons.
Tharsis	480,000 „
S. Domingo	280,000 „
Grandola	20,000 „
Other mines	220,000 „
	<hr/> 2,000,000 „

The following analyses represent the average quality :—

	Rio Tinto.			S. Domingo.		Tharsis. Bartlett.
	Cumenge.	Caron.	Rivista Min. 23.	Pattinson.	Bartlett.	
Sulphur	48·00	50·7	49·00	49·9	49·80	47·50
Iron	40·00	41·3	43·55	41·41	43·55	41·92
Copper	3·42	3·5	3·20	2·46	3·20	4·21
Lead	0·82	0·93	0·98	0·93	1·52
Zinc	trace	0·35	0·44	0·35	0·22
Arsenic	0·21	0·47	0·55	0·47	0·38

Fulton (J. Soc. Chem. Ind. 1886, p. 296) describes at length the elimination of arsenic in the local treatment of Spanish pyrites for copper precipitate.

Recently a new mine of non-cupreous pyrites has been opened in the Huelva district, that of Aguas Teñidas (belonging to the Société Maritime et Commerciale at Antwerp). It is extremely rich, its composition being :—

* The explosive pyrites from Goshen Copper Mine, near Scull Harbour, County Cork, is said to contain confined carbon dioxide and water (Blount, in J. Soc. Chem. Ind. 1885, p. 674).

Iron	46·60 per cent.
Sulphur	53·15 „
Silica	0·20 „
Arsenic	} traces.
Copper	
Selenium, Silver, Gold ...	

It is sold both in the state of lumps and smalls. It is said to burn very easily down to 0·5 per cent. of sulphur, so that the cinders, which contain 68·5 per cent. of metallic iron, and no copper, phosphorus, lead, or zinc, are very valuable for blast-furnaces. It is asserted that the annual sales will soon amount to 200,000 tons.

The *United States of North America* are very rich in pyrites. The principal mines worked at present are the following (from *United States' Mineral Resources*).

In New Hampshire: the Milan mines, Coos County. The ore is of excellent quality, and is now sorted into two grades, of the following composition:—

	No. 1.	No. 2.
Sulphur	46·0	35·0
Copper	3·7	5·0
Iron	40·0	30·5
Silica	6·2	25·5
Zinc	4·0	8·0
Arsenic	0	0

No. 1 is in special favour, but No. 2 burns very well, and is readily bought. Smelting-works exist for extracting the copper and silver.

New York: 2000 tons were raised at Hermon, County St. Lawrence; sulphur contents, 38·0 per cent. Another mine at Ulster County, with 39 per cent. ore, was worked till stopped by an inrush of water.

Massachusetts: the mines of the Davis Company, at Charle-mont (Mass.), are only about 130 miles from New York, in the centre of a network of railways. The ore contains 48·5 per cent. sulphur, no trace of arsenic, antimony, or cobalt, little or no zinc, lead, or calcium, 1·5 copper, 45·3 iron, and less than 3 per cent. of silica. It is granular, easily broken by hand, and burns down

to 3 per cent. of sulphur. In 1884, about 30,000 tons were got; it was burned in four works.

Virginia: Arminius Copper Mines Company and Sulphur Mines Company, both in Louisa County. The ore contains 49·5 per cent. sulphur, 0·5 copper, 43·5 iron, 6·4 silica, &c. Annual output, 13,000 tons (in 1885).

Georgia: Dallas mine, Paulding County; the ore contains: sulphur 40 per cent., copper 2·75 (sometimes up to 11 per cent.), silica 8 per cent.

The absence of arsenic in most American pyrites (as far as it is now worked) is a remarkable feature.

The production of pyrites in the United States has amounted to the following quantities:—

Year.	tons.
1882.....	12,000
1883.....	25,000
1884	35,000
1885	40,000
1886.....	55,000
1887.....	52,500

In 1882 there were only two works burning pyrites in the United States; in 1885 already 19 (Boston and Eastern District 6, New York District 7, Philadelphia District 2, Baltimore and Southern States 3, Western District 1), with a total consumption of 91,400 tons, part of which came from Spain and Portugal. In 1886 the total consumption was 112,000 tons (about half of which was imported from abroad), and it was not expected that it would rise very much, there being a disinclination on the part of manufacturers to change from the use of sulphur to that of pyrites, owing to the fact that the change involves new experiments and also greater care, although the profits are greater with pyrites than with sulphur. (This statement, not very creditable to the skill and enterprise of those concerned, is found in the official 'Mineral Resources of the United States,' 1887, p. 609.)

In *Canada* there are two mines: the Albert mine and the Crown mine. They supplied the first pyrites used in the United States for making oil of vitriol. Sulphur 40·0, iron 35·0, copper 4·0, silica 20·0. Output in 1885, 35,000 tons.

*Statistics of the World's Production and Consumption of
Pyrites for 1886.*

(From 'United States' Mineral Resources,' year 1886, p. 657.)

Countries.	Consumed for acid-making where mined.	Imported for acid-making.	Exported for acid-making.
	tons.	tons.	tons.
Spain and Portugal	771,419
United Kingdom	36,500	592,000
France	182,700	67,200
Germany	132,000	73,000*
Belgium	28,000	22,000
Norway and Sweden	46,000
United States	55,000	57,000
Canada	37,000

The total quantity of pyrites used in the production of sulphuric acid throughout the world, during 1886, was at least 1,265,000 tons (not reckoning, of course, the large quantity of pyrites, amounting to more than a million tons, roasted in Spain near the mines without turning the gases to use).

Prices obtained in the Liverpool district for pyrites, when sold for sulphur only :—

Year.	Prices per unit of sulphur.	Year.	Prices per unit of sulphur.
1861	10·85 <i>d.</i>	1870	6½ <i>d.</i>
1862	9·625	1871	7½
1863	8	1872	7½
1865	9	1873	7½
Jan. 1886	9½	1876	5½
Mar. 1866	11·02	1877	4½
Jan. 1868	10·04	1878	4½
June 1868	9½	Jan. 1879 to }	5½
Oct. 1868	8	Dec. 1884 }	
Jan. 1869	7	1885 to }	3 to 3½
June 1869	8	1887 }	

(E. K. Muspratt in J. Soc. Chem. Ind. 1886, p. 405.)

* This figure is probably too low. According to official sources, the importation of pyrites and alum-ore into Germany in the year 1889 amounted to 216,164 tons, and of this quantity "alum-ore" would form but a small portion.

Average Composition of the World's Pyrites.
(From 'United States' Mineral Resources,' 1886, p. 652.)

Localities.	Sulphur.	Iron.	Copper.	Arsenic.	Zinc.	Lead.	Carbonate and Sulphate of Ca and Mg.	Silica.
Milan mine, New Hampshire, No. 1	46.00	40.00	3.75	trace	4.00	none	...	6.25
" " No. 2	35.00	30.50	5.00	none	8.00	21.50
Davis mine, Mass.	49.27	45.30	1.47	trace	3.83
Elizabeth mine, Vermont	33.00	50.00	3.50	13.50
St. Lawrence Company, New York	38.00	31.00	3.00	25.00
Arminius mine, Va.	46.00	44.50	2.10	7.40
Capelton, Canada	40.21	35.20	5.10	trace	8.00	12.00
Rio Tinto, Spain	48.50	40.92	4.21	0.33	0.22	1.52	0.90	3.46
Tharsis, Spain.....	49.90	42.55	3.10	0.47	0.35	0.93	0.87	2.20
S. Domingo, Portugal	49.07	44.28	3.25	0.38	0.93	2.59
Swedish mines.....Average	38.05	42.80	1.50	none	5.09	12.56
Norwegian "	46.15	44.20	2.10	trace	1.20	...	2.50	3.65
French "	46.60	39.70	none	0.20	13.50
German "	45.60	38.52	...	0.95	6.00	0.74	...	8.19
Belgian "	42.80	36.70	...	0.20	0.40	0.92	5.45	12.47
English "	34.34	32.20	0.80	0.91	1.32	0.40	...	30.03
Irish [?] "	47.41	41.78	1.93	2.11	2.00	4.77

Proportional value of poor and rich Pyrites.

It is no matter of surprise that the rich and at the same time well-burning Spanish ores, and those ores similar to them elsewhere, where they could be imported, have driven the poor ores out of the field. An ore of 35 per cent., like that from Wicklow, even for the same weight of sulphur, has much less value than a 45-per-cent. ore. The wages for breaking and burning the ore in both cases must be ruled by the gross weight of the ore, and consequently for equal weights of sulphur come to much more with poor than with rich pyrites; moreover, under conditions otherwise equal, the unburnt sulphur in the cinders is the same by weight. If, for instance, 5 per cent. of sulphur are left in the cinders, this amounts with 35-per-cent. ore to $\frac{5}{35} = \frac{1}{7}$; with 45-per-cent. ore to only $\frac{5}{45} = \frac{1}{9}$; the proportion to be kept in view is accordingly not $35 : 45 = 7 : 9$, but $30 : 40 = 3 : 4$. Furthermore, the same holds good of cost of plant and repairs, and of wages, and, lastly, since the poor ores generally contain no copper, also of the cost of removing the cinders.

Therefore, unless the burning is nothing but a preparation for the metallurgical treatment, where the sulphur is quite a secondary matter, the ores poor in sulphur are always avoided as much as possible.

Analysis of Pyrites.

In the analyses of pyrites for technical purposes, in the first instance their percentage of sulphur is taken into account; and it is therefore mostly the custom to estimate only this and, perhaps, also the moisture. If the ore has afterwards to yield copper, this must of course also be regarded; but where the copper, as is mostly the case, is not bought by the vitriol-maker, but the cinders are returned to the seller, the estimation of copper is generally omitted in the chemical works as unnecessary. This restriction to the estimation of sulphur ought, however, only to take place with pyrites from well-known localities, whose general composition and properties are well known, and where the salient point is only the percentage of the most important constituent, viz. the sulphur. Each cargo, when each portion of a cargo going to a separate buyer, is sampled in the presence of both the buyer's and seller's agents, according to well-understood rules; the sample is broken up, reduced, and

sealed up in bottles, which are sent to an analytical chemist (generally mentioned in the contract note); this chemist's certificate rules the price to be paid for the pyrites down to $\frac{1}{4}$ per cent. If, for instance, a sale has been made at 6*d.* per "unit," this means that for each per cent. of sulphur found the sum of 6*d.* per ton is paid; thus for $48\frac{1}{4}$ per cent. of sulphur $48\frac{1}{4} \times 6d. = 24s. 1\frac{1}{4}d.$ per ton. The ton is generally calculated = 21 cwt.; that is to say, the buyer receives an allowance in weight of 5 per cent.

The first treatment of the pyrites in analyses, in the majority of cases, is by the *wet* way, by fuming nitric acid or aqua regia; but the prescriptions differ in details. The solution has frequently been made, from Fresenius's prescription, by means of red fuming nitric acid, which it is sometimes difficult to obtain free from sulphuric acid, and which is unpleasant to handle. In lieu of this sometimes chloride of potash along with hydrochloric acid, or, still better, with nitric acid of 1.36 sp. gr., have been used. The author has always found the best, safest, and cheapest way to be that by aqua regia, made from 1 part of fuming hydrochloric acid and 3 or 4 parts of nitric acid of 1.36 to 1.4 sp. gr. The mineral is converted into an impalpable powder and passed through the finest silk gauze; the triturating ought to be done first in a steel mortar or by wrapping it up in paper and smashing with a hammer, and then in an agate mortar, *not* in a porcelain or Wedgewood mortar. The powder is treated with about 50 parts of aqua regia; if no reaction takes place at once, it should be gently heated on a water-bath till the reaction sets in; but then the beaker should be removed instantly from the water-bath, and only replaced when the reaction slackens: thus the solution is generally complete in 10 minutes. The operation, of course, has to be done in a large beaker, or, still better, in an Erlenmayer's flask covered by a funnel or a watchglass, lest any loss should take place by spurting; and the work must be done in a draught-place, on account of the mass of acid vapours given off. If the solution should not be perfect after heating some time, some more aqua regia has to be added and the heating continued; but mostly this will be caused by the powder not being sufficiently fine, and the analysis in this case cannot easily be finished. In this way of decomposing the ore, which is both quick and safe, the disagreeable separation of sulphur happens very rarely.

The residue from the solution will contain silica and silicates, perhaps a little lead or barium, both as sulphates. Although their

sulphur is thus not estimated, no harm is done, as it is anyhow valueless to the manufacturer. Lead sulphate is pretty soluble in concentrated acids, but it is almost entirely precipitated again by the immediately following treatment.

At all events the whole of the nitric acid present must be destroyed or removed, because the estimation of sulphuric acid by barium chloride in the presence of nitric acid or its salts gives results much in excess of the truth. The whole is therefore evaporated to dryness on the water-bath with an excess of hydrochloric acid, by which at the same time all silicic acid dissolved is made insoluble. The mass is again moistened with strong hydrochloric acid; and if on gently heating no yellow vapour and no smell of nitrous products are perceived, it is diluted with hot water and the solution filtered from the residue. Care must be taken not to employ too much hydrochloric acid, as barium sulphate is not quite insoluble in hot concentrated acids; on the other hand, enough acid must be present to dissolve all salts of iron, which cannot be doubtful if the colour and behaviour of the residue are observed. The clear solution is brought to *full boiling*; and to it during boiling a *hot* solution of barium chloride is added. Lest too great an excess of this be used, it is preferable to use a measured quantity of a concentrated solution of known strength, but more than sufficient for precipitating all the sulphuric acid present. If the process is carried out as described here, the barium sulphate settles down completely in a few seconds, leaving a perfectly clear liquid, and nothing of the precipitate passes through the filter. It is quite unnecessary to allow a long time for the settling. If the operation is carried on as described, the filtrate never becomes cloudy afterwards; on the other hand, the work is extremely hastened by filtering the liquid in the boiling-hot state, say 15 or 20 minutes after precipitation. A Bunsen's filter-pump acts rather too strongly in this case; but it is very useful to employ a simple contrivance indicated many years ago by Piccard, which does excellent service in other analytical operations, viz. a glass tube attached to the funnel by means of an elastic joint, with a loop, causing a continuous jet of liquid to issue at the bottom (fig. 4). The straight part below the loop may be 8 or 10 inches long; the filter must be pressed tight to the sides of the funnel to prevent any air being sucked in. When this contrivance is used, which does not act so violently as a Bunsen pump, the liquid, so long as there is not too much precipitate in the filter, runs through in a continuous jet.

At first only the clear liquid is poured off as completely as possible from the dense granular precipitate; this is covered with *boiling water*, acidulated with a few drops of hydrochloric acid; the liquid is boiled for a few moments, and can be decanted again in about two minutes' time. This is repeated another twice or three times, but without adding any more hydrochloric acid; the precipitate is washed onto the filter, and after very little washing the filtrate will be found perfectly neutral and free from dissolved matters. The filter is dried, the precipitate taken out, and the filter burnt, preferably in a platinum crucible laid on its side; then the precipitate is put in and ignited, not too strongly; and for each 100 parts of barium sulphate found 13.734 parts of sulphur are calculated. The ignited barium sulphate ought not to cake together; on moistening, it ought not to give an alkaline reaction; and on heating with dilute hydrochloric acid and filtering, no barium salt ought to be found in the solution.

In generally happens, even if the solution before precipitation was rather strongly acid, that the precipitate is stained yellowish by precipitated ferric oxide or basic ferric sulphate, which cannot be removed even by boiling with dilute hydrochloric acid.

Although this proves the presence of a foreign substance in the barium sulphate, which ought to make the result too high, yet it is found in practice that the results are always too low. The cause of this apparent anomaly has been studied by Jannasch and Richards (Journ. f. prakt. Chem. [2] xxxiv. p. 321), who found that in the presence of iron a barium-ferric sulphate is precipitated, which on ignition slowly loses a portion of its sulphuric acid. If the ignition is carried on very persistently, the error thus produced may amount to a full per cent. of sulphur or upwards; but I have shown, in the paper to be quoted below, that with the ordinary mode of ignition it does not exceed 0.18 per cent.; hence the above-described method is always available where perfect

Fig. 4.



accuracy is not required, and a speedy completion of the test is a consideration. Westmoreland (*J. Soc. Chem. Ind.* 1887, p. 84) even contends that its results entirely agree with those obtained by my new method (an opinion to which I must demur).

Where, however, the greatest possible accuracy and freedom from error is required (and this is the case when testing an average sample of pyrites representing a whole cargo, or a large portion of such), it is necessary to remove the disturbing influence of the iron. This can be done in two different ways, by the dry and by the wet method. The dry method is that recommended by Fresenius (*Zeitsch. f. anal. Chemie*, xvi. p. 335). He prescribes to decompose the pyrites by fluxing it with 20 parts of a mixture of 2 parts of dry sodium carbonate entirely free from sulphate, and 1 part of potassium nitrate, conducting carbonic acid into the solution for the precipitation of lead, boiling the residue with a solution of sodium carbonate and then with water, acidulating with hydrochloric acid, and repeatedly evaporating for the expulsion of nitric acid, after which the process is carried on as usual, the precipitation taking place by barium chloride. This process is much more troublesome and tedious than that to be described below, which employs the wet method. Another objection to it is that it estimates not merely the sulphur of the iron and copper sulphides, but also that of galena and of barium sulphate, which are entirely useless to the manufacturer of sulphuric acid *. Moreover, the platinum crucibles are strongly acted upon, and coal-gas cannot very well be employed in the operation of decomposing the pyrites, as its sulphur would cause an error in the test. Hence it is prescribed to use spirit-lamps of a special shape, calculated to yield the necessary heat. [The use of spirit-lamps can be practically avoided by placing the crucible in a round hole made in a piece of asbestos cardboard, in which case the products of the combustion of coal-gas are carried off sideways.]

Hayes ('*American Chemist*,' v. p. 271) describes a method of decomposing pyrites with alcoholic soda and lime, the advantages of which are in no way evident.

Fahlberg and Iles (*Ber. d. deutsch. chem. Ges.* xi. p. 1187) recommend fluxing the sulphur-ore with caustic potash (25 grams to 0.1 gram of S) in a silver crucible for 15 to 20 minutes, lixiviat-

* Concerning the action of nitric acid on lead sulphate, see my experiments detailed in *J. Soc. Chem. Ind.* 1887, p. 96.

ting the mass, oxidizing the lower oxides of sulphur by bromine-water, and precipitating by barium chloride.

Clark (J. Soc. Chem. Ind. 1885, p. 329) heats the pyrites with a mixture of sodium carbonate and magnesia to a dark red heat; the resulting mass is lixiviated with water whilst passing in carbonic acid, and the sulphuric acid estimated in the usual way. J. Pattinson (*ibid.* p. 724) shows that this method gives exactly the same result as my method (of course, only in cases where barium sulphate and galena are absent, which militates against Clark's process).

Looking at the great desirability of retaining the decomposition of pyrites in the wet way, I have worked out a method for doing so without incurring the error caused by the presence of iron. This method was first described in the *Zeitsch. f. anal. Chemie*, 1880, p. 419, and has been very generally accepted for the assaying of pyrites between buyer and seller. Objections made to the accuracy of that process by Jannasch and Richards (*Journ. f. prakt. Chem.* [2] xxxix. p. 321) have been withdrawn by themselves (*ibid.* xl. p. 236), and have been completely refuted by experiments made in my laboratory by two independent investigators (*Zeitsch. f. ang. Chemie*, 1889, p. 473). The process, as it will be described now, may hence be considered as the most accurate known for the estimation of sulphur in pyrites, where it is desirable *not* to include galena and heavy-spar, and it is at the same time very easy and speedy of execution, if the following directions are accurately observed.

About 0.5 grm. of pyrites is heated with about 10 c. c. of a mixture of 3 vols. nitric acid (spec. grav. 1.4) and 1 vol. strong hydrochloric acid, both ascertained to be absolutely free from sulphuric acid. The operation is carried on as described above, in such manner that no loss by spurting takes place. The mixture is heated up now and then, till the decomposition is complete, and is then evaporated to dryness in a water-bath. Now add 5 c. c. hydrochloric acid, evaporate once more (no nitrous fumes ought to escape now), add 1 c. c. concentrated hydrochloric acid and 100 c. c. hot water; filter through a small filter and wash with hot water. The insoluble residue may be dried, ignited, and weighed. It may contain, besides silicic acid and silicates, the sulphates of barium, lead, and even calcium, whose sulphur, as being useless, is purposely neglected. The filtrate and washings are saturated with

ammonia, avoiding much excess of it; the mixture is kept at a moderately warm temperature for about 10 minutes (at the expiration of which time it ought still to smell of ammonia very distinctly, not merely faintly), and the precipitated ferric hydrate is filtered off while the liquid is still hot. For this purpose funnels must be used, made at an angle of exactly 60° , whose tube is not too wide and is *completely* filled by the liquid running through; or else a Piccard's tube (comp. above, p. 53), or a filter-pump is employed. The filtering-paper ought to be sufficiently dense, but act rapidly; the filter must be adapted to the funnel so that no air-channel is left between paper and glass. The hot liquid is first decanted from the ferric hydrate, and the latter is then washed onto the filter with boiling water. The washing is continued with hot water in such manner that each time the whole precipitate is thoroughly churned up, and no channels are formed in the mass. When acting on these instructions, the whole operation can be performed in from half to one hour, and no trace of sulphuric acid is retained in the precipitate. The total bulk of the filtrate and washings need not exceed 200 or 250 c. c., which saves concentrating the liquid by evaporation. The end of the washing is indicated by the fact that 1 c. c., on adding barium chloride, shows no opalescence even after a few minutes.

The clear liquid, which now contains all the sulphuric acid combined with ammonia, is acidulated with pure hydrochloric acid in very slight excess, heated to boiling, the burner removed, and 20 c. c. of a 10-per-cent. solution of barium chloride, previously heated, is poured in. This quantity, which suffices in any case for 0.5 gram pyrites, is roughly measured off in a test-tube provided with a mark, and is heated in the same tube. After precipitation, the liquid is left to stand for half an hour, when the precipitate should be completely settled. The clear portion is now decanted, and the washing continued by decantation with boiling water, as mentioned on p. 54, where the mode of igniting the precipitate is also described. The ignited precipitate should be a perfectly white and loose powder, one part of which is equal to 0.13724 sulphur.

The accuracy of the Author's new method and its complete accordance (in the case of pure ores) with the fusion method of Fresenius has been proved by Pattinson (Journ. Soc. Chem. Ind. 1890, p. 21), who points out how much more convenient is the former than the latter.

Some chemists prefer to the aqua regia above described a solution of bromine in hydrochloric acid; but I have not found this to answer very well. Drown (Chem. News, xliii. p. 89) heats the pyrites with a solution of caustic soda of spec. grav. 1.25, adds cautiously bromine in excess, acidulates with hydrochloric acid and evaporates to dryness.

In lieu of the estimation of sulphuric acid by weight, some chemists prefer titration by means of a standard solution of barium chloride. This was first proposed by Wildenstein (Zeitsch. f. anal. Chemie, i. p. 432), and afterwards, especially for the analysis of pyrites, by Teschemacher and Smith (Chem. News, xxiv. pp. 61, 66; comp. also Glendinning and Edger, *ib.* p. 140). Although this process, notwithstanding some assertions to the contrary, is most certainly no more accurate than the gravimetric process, and in most hands is less so, and is not used by many chemists in important cases, we shall take this opportunity of describing the estimation of sulphates by titration with barium chloride in its simplest form, such as is used at some works in testing black-ash, &c.; it is also used sometimes in testing pyrites, blende, burnt-ore, &c. for purposes where no great accuracy is required.

The liquid is brought to the boil in a porcelain dish, barium-chloride solution is added from a burette; from time to time a few drops are taken out with a glass tube, filtered through a miniature filter onto a glass plate resting on a black background, upon which

Fig. 5.



a number of drops both of dilute sulphuric acid and of barium chloride have been put. If the filtrate still gives a cloudiness with a barium-chloride drop, easily visible on the black ground, the little filter is thrown back into the dish, more barium-chloride solution is

added from the burette, another test is made, and so forth. The end is attained when a filtered drop gives an extremely small cloudiness both with a drop of barium chloride and with one of sulphuric acid. The work is very much expedited by the following contrivance, proposed by Wildenstein and shown in fig. 5. The acidulated solution is poured into a vessel, A, made of a bottle by removing the bottom, or a small tubulated jar, through whose cork passes a bent tube B, provided at the lower end with the pinchcock *l*, at the upper end with a bent-down funnel *t*. The latter (which must be bell-shaped) is closed by two disks of filtering-paper and a piece of linen gauze tied over all; and the liquid must cover the whole tube. This arrangement permits of withdrawing at will small filtered samples of a few drops each, which are run into a test-tube and tried with a drop of barium-chloride solution. It must, of course, not be omitted first to run a few c. c. out of the tube B and back into the jar A before taking the sample for testing; and the contents of the test-tube must be always put back into A, not to waste too much substance. If by accident the point of finishing the reaction has been overstepped, one or more c. c. of titrated sulphuric acid are put in, and are afterwards deducted from the result.

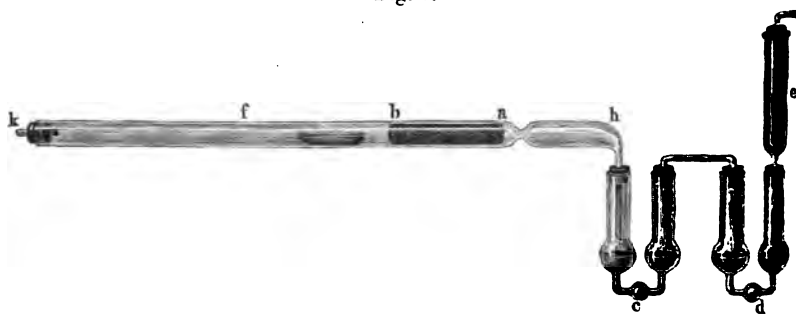
C. and J. Beringer effect the titration by barium chloride after addition of sodium acetate and acetic acid (Chem. News, lix. p. 41).

Various other volumetric methods for the estimation of sulphates, by Carl Mohr, Ad. Clemm, Wildenstein (2nd method), Schwarz, Pappenheim, are described in the treatises of Fresenius and Mohr; but they are more complicated and no more accurate than the direct titration with barium chloride as just described. We, therefore, mention only one of the newest methods of this kind. This is the method proposed by Wilsing (Chem. Ind. 1886, p. 25), a slight but apparently useful modification of those just mentioned. He precipitates a neutral solution of the sulphate or solution containing such, boiling in a porcelain dish, with a 4-per-cent. barium-chloride solution of known strength; he then adds a few drops of an alcoholic solution of phenolphthalein and a 2-per-cent. solution of sodium carbonate: as soon as the last part of barium chloride has been precipitated as carbonate the colour turns red, so that the soda used is a measure for the sulphate originally present. If the solution to be tested is either acid or alkaline, it must be made neutral by sodium carbonate or hydrochloric acid, phenolphthalein being used as indicator here as well.

L. W. Andrews (Amer. Chem. J. 1889, p. 567, & Chem. Zeit. 1889, Rep. p. 39) proposes the following method for estimating sulphuric acid combined with bases. The solution is diluted till it contains no more than 2 per cent. SO_3 , is almost neutralized and brought to a boiling heat. Now a solution of pure barium chromate in hydrochloric acid is added, and then ammonia, the excess of which is removed by boiling. The solution is filtered while hot, and is washed at once. Now a quantity of chromic acid, equivalent to the sulphuric acid originally present, will be in solution; this is estimated by adding potassium iodide and strong hydrochloric acid, and titrating with decinormal thiosulphate-solution (1 c. c. = 12.654 mg. I = 2.662 mg. SO_3). It is claimed that this method is more quickly executed than the gravimetric process, and is at least as accurate; but both of these assertions are doubtful.

Several methods have been proposed for estimating the *available sulphur* of sulphur ores—that is, that portion of it which passes into the chambers in the shape of SO_2 and SO_3 . Thus W. G. Mixter (Amer. Chem. J. ii. p. 396) burns the pyrites in a current of oxygen, and passes the vapours into bromine water containing some hydrochloric acid and an excess of bromine. A similar process is recommended by Zulkowsky (Wagner's Jahresb. 1881, p. 160), both for testing pyrites and spent oxides of gas-works. The latter is always contaminated with sawdust, tarry matters, and variable quantities of lime, which retains part of the sulphur in

Fig. 6.



burning, whence an estimation of the total sulphur is quite useless for practical purposes. The process takes place in a combustion-tube (fig. 6), 2 feet long, narrowed at *a*, and drawn out at the end

into a long tube, not too thin, and bent downwards. Between *a* and *b* there is a layer of platinized asbestos (see below), 8 to 10 inches long, and at a distance of 3 or 4 inches from this a porcelain boat with about 0.4 grm. of spent oxide or pyrites. The end of the tube at *k* is connected with an oxygen gas-holder. The absorption of the vapours takes place in the two 3-bulb tubes *c* and *d* (5½ inches high) and the tube *e*, filled with glass-wool. The absorbing liquid is made by dissolving 180 grams caustic potash (purified with alcohol from sulphate) in water, adding 100 grams bromine, taking care to keep the mixture cool, and diluting to 1000 c. c. 30 c. c. of this suffice for estimating 0.5 grm. sulphur. The tube *e* ought also to be moistened with it. First heat the portion of the tube between *a* and *b*, passing moist oxygen through it at the same time; then heat the boat from the right to the left; lastly the tube, up to the place *f*. The current of gas must be much stronger than for an organic analysis, lest any sulphur should escape unburnt, but not strong enough to draw off any SO_2 unabsorbed. So long as any dew appears at *h*, it must be driven into the receiver with a Bunsen burner. When this ceases (usually in about an hour), the experiment is finished. The receivers are then taken off, washed out, and the acid remaining in *h* is recovered by aspirating several times water through it. All the liquids are united, supersaturated with hydrochloric acid in order to decompose the potassium hypobromite, heated, concentrated if necessary, and the sulphuric acid is precipitated by barium chloride in the usual manner.

Jannasch (Journ. f. prakt. Ch. [2] xl. p. 237) heats pyrites in a mixture of air or oxygen and nitric-acid vapours; the vapours of SO_2 and SO_3 are absorbed in bromine water. [It must not be forgotten that in the presence of nitric acid the barium sulphate is never free from nitrate, and that hence all nitric acid must be removed previously. I would, therefore, propose to use in that class of processes hydrogen peroxide as an absorbent, which is very efficient and requires no special precautions; in this case the acids absorbed can be estimated by titration with the standard alkali.]

Graeger (Dingl. Journ. ccxli. p. 53; Fischer's Jahresb. 1881, p. 161) heats pyrites with reduced metallic iron, decomposes the FeS formed by dilute hydrochloric acid, and titrates the H_2S evolved by passing it into a solution of iodine.

Expeditious assays of pyrites have been proposed in many ways, but none of them is sufficiently accurate to be employed for estimating the sulphur in fresh pyrites, and some of them are not even accurate enough for testing the sulphur remaining in burnt-ore.

The so-called *mechanical pyrites assay* of Anthon (Dingl. Journ. clxi. p. 115) is too rough and unreliable even for very simple purposes. (Comp. 1st ed. of this work, i. p. 108.)

In the Freiberg works 1 gram of finely ground pyrites is mixed with 2 grams sodium carbonate and 2 grams saltpetre; the mixture is fluxed in a small iron dish in a red-hot muffle-furnace, dissolved in hot water and filtered into a beaker in which there is hydrochloric acid for saturating the soda in excess. Then the filtrate is brought to boiling, and the sulphuric acid estimated by a standard solution of barium chloride, preferably by Wildenstein's method (*supra*, p. 59). Liebig (Post's Techn. chem. Analyse, 2nd ed. i. p. 677) recommends this method as a quick and easy one, where no great accuracy is required.

In the method of Pelouze (Compt. Rend. liii. p. 685; Ann. de Chim. et de Phys. [3] lxiii. p. 415) the finely powdered pyrites is mixed with chlorate of potash, common salt, and an exactly weighed quantity of sodium carbonate, and ignited, which can be done in an iron spoon. The fluxed mass is dissolved in water, filtered, the residue washed, and the soda not converted into sulphate estimated alkalimetrically. This process continued to be recommended in French treatises till very recently, although its inaccuracy was established and the sources of error partly demonstrated by many chemists, such as Barreswil, Bottomley, Bocheroff, Lunge, and especially Kolb ('Notes sur l'Essai des Pyrites de Fer'). Kolb found the sources of error on the one hand in the formation of sodium silicate, on the other hand in the decomposition of potassium chlorate in the presence of ferric oxide into chlorine, oxygen, and caustic potash. New experiments made in my laboratory by Mr. Rey have equally proved the method to be wrong, even if the "constant error" of 1 to $1\frac{1}{2}$ per cent., admitted by Pelouze, is taken into account. A principal objection is the difficulty of avoiding the mechanical loss by spurting in the fluxing process.

This fault is avoided in the plan proposed by Kolb (J. pharm. Chim. [4] x. p. 401), which, however, is only intended for testing

burnt-ore. Kolb mixes 5 or 10 grams of this with 5 grams pure sodium carbonate and 50 grams cupric oxide, heats about 15 minutes in an iron capsule to a dark-red heat, with stirring, lixivates the melted mass, and estimates the unconsumed soda volumetrically. The trials made in the Author's laboratory showed that there is no spurting, but that the heating must not be prolonged too much, in order to avoid the formation of silicates. The lixiviation of the large bulk of cupric and ferric oxide is tedious, and the method is somewhat costly, as it requires 50 grams of cupric oxide for each test, nor are the results very satisfactory (see below).

The best method for testing burnt-ore is that proposed by J. Watson (J. Soc. Chem. Ind. 1888, p. 305). 2 or 3 grams of pyrites cinders are mixed with 1 or 2 grams of sodium bicarbonate of known titre; the mixture is heated in a nickel, porcelain, or platinum crucible by means of a small Bunsen flame for 5 or 10 minutes, stirred up, heated once more for 15 minutes with a somewhat stronger flame, treated with hot water, filtered and washed. The solution is titrated with hydrochloric acid and methyl-orange; the loss of titre in comparison with the original one is equal to the sulphate formed. The escaping carbonic acid keeps the mass porous; there is no spurting, and the lixiviation of the small bulk of the mixture is easy and expeditious.

Experiments made in the Author's laboratory (Zeits. f. ang. Chem. 1889, p. 239) showed that Watson's method yielded results closely agreeing with those obtained by accurate gravimetric methods, whilst the method of Pelouze, even with burnt-ore, yielded too low results, and that of Kolb was no more reliable.

Estimation of other constituents of Pyrites.—Usually it is sufficient to estimate the sulphur in a pyrites whose nature is otherwise known. If, however, the pyrites is of unknown composition, its value for acid-making can only be estimated by a complete determination of all its constituents according to the rules of mineral-analysis. If it contains, for instance, *calcium carbonate*, this on burning will retain its equivalent of sulphuric acid; if *calcium sulphate* is present from the first, its sulphuric acid has to be deducted from the whole quantity of sulphur found. If *lead* has been found, an equivalent of sulphur must be considered as practically lost; and the same is the case with *zinc*,—because the sulphates of both metals are hardly or not at all decomposed at the

temperature of a pyrites-burner. Frequently *arsenic* will also have to be sought for; and even *silica* may be of importance—in the first instance because in the presence of much silica “explosive” properties of the pyrites must be feared (see p. 46), and secondly, in the case of cupreous pyrites, because silica lessens the value of the cinders. Even *silver* and *gold* are sometimes sought for (comp. Chem. News, xxvi. p. 63, xxxiv. pp. 94, 132, 152, 172); but it cannot be said that the quantities found have any influence on the commercial value of pyrites.

It is not our task here to treat of the estimation of all these substances, no more than of that of the *copper* which, in the majority of cases, represents a large portion of the value of pyrites*. We make an exception only with *arsenic*, because special methods for estimating this in pyrites have been worked out which are not found in the ordinary text-books.

The process employed at Freiberg is that worked out by Reich, and is as follows. Digest about 0.5 gram of finely pulverized pyrites in a porcelain crucible, covered with a watch-glass, with concentrated nitric acid at a gentle heat, until the residue assumes a lighter colour and the separated sulphur has turned a pure yellow. After decomposition, heat the crucible on a sand-bath to get rid of the excess of acid, but not to dryness. Add 4 grams of sodium carbonate, dry completely on the sand-bath, add 4 grams of potassium nitrate, and heat the mass until the contents of the crucible have been in quiet fusion for ten minutes. Extract the cooled mass with hot water, and filter; the filtrate contains all the arsenic as sodium arseniate. Acidify with a little nitric acid, keep for two hours on a sand-bath to get rid of the carbon dioxide, add a sufficient quantity of a solution of silver nitrate, and neutralize carefully with dilute ammonia. The reddish-brown precipitate of silver arseniate is filtered, washed, dried, taken off the filter as well possible, the filter is incinerated in a muffle, the precipitate put to it, a sufficient quantity of assay lead is added, and the silver estimated by cupellation. 100 parts of silver correspond to 23.15 of arsenic.

Leroy M. McCay has modified and greatly simplified this method (Chem. News, xlviii. p. 7) by estimating the excess of silver used by

* For these substances, see Lunge and Hurter's 'Alkali-maker's Pocket-book'; also a very extensive paper by Westmoreland, J. Soc. Chem. Ind. 1886, p. 31, and criticisms on the same, p. 277.

Volhard's method. Later on (Amer. Chem. J. viii. no. 2), the same author recommends as preferable another plan, namely dissolving the Ag_3AsO_4 in dilute ammonia, and either estimating the silver by Volhard's volumetric method (precipitation with ammonium thiocyanate), or evaporating, drying, and weighing the total in a thin platinum dish. If the arsenic is to be precipitated as pentasulphide, which is otherwise a tedious operation, McCay recommends (Amer. Chem. J. ix. no. 3, and x. no. 6) to place the solution in a flask with a well-fitting stopper, acidify with HCl , and dilute with freshly boiled water till the flask is nearly full, pass in H_2S to saturation, insert and fasten down the stopper, and place the whole in a water-bath for an hour. At the end of that time all the arsenic will be precipitated as pentasulphide, As_2S_5 , containing no free sulphur.

Clark (J. Soc. Chem. Ind. 1887, p. 352) recommends the following method as specially adapted for estimating very small quantities of arsenic in pyrites rich in sulphur. Mix 3 grams of pyrites in a platinum crucible with four times as much of a mixture of calcined magnesia and sodium hydrate, heat for about 10 minutes over a moderately low Bunsen flame, extract the shrunk mass with boiling water, acidify the solution with hydrochloric acid (which evolves much H_2S), boil for a few minutes, and saturate with H_2S , when all the arsenic will be thrown down as sulphide; wash the precipitate, extract the sulphide of arsenic with ammonia, evaporate the solution to dryness, dissolve in strong nitric acid, and estimate the As as ammonio-arsenate of magnesia, or else by silver solution as above described. Or else the calcined mixture, after neutralizing it with HCl , as above mentioned, is reduced by cuprous chloride, and the liquid is slowly distilled into water, repeating this operation twice with strong HCl , which will cause all the arsenic to pass over as AsCl_3 , which can be either precipitated by H_2S or titrated by iodine. Clark points out the necessity of carefully testing all the reagents employed for arsenic, of which he had found as much as 0.02 per cent. even in commercial caustic soda.

Nahnsen's process (Chem. Zeit. xi. p. 692; abstr. J. Soc. Chem. Ind. 1887, p. 564) does not offer any special advantage. The process described in detail by H. Fresenius (Zeitsch. f. anal. Chemie, 1888, p. 34) is no doubt very accurate, but lengthy and troublesome.

3. OTHER METALLIC SULPHIDES.

Pyrites proper has hardly any other application than that for sulphuric-acid making, and it is got almost exclusively for this purpose. In the case of cupreous pyrites the sulphur constitutes only a portion, but a very considerable one, of its value. The working of poor ores, such as those in question here, would not pay, apart from the noxious effect of the gas produced in calcining the ore, unless the price of the ore were very moderate; and this is only possible by the acid-makers paying on their part for the ore, which they can do very well, as most kinds of cupreous pyrites behave very well in the burners, and yield quite as much acid in proportion to their percentage of copper as the non-cupreous ores.

The case is different with most other sulphuretted ores occurring in smelting-operations, such as blende, galena, the many mixed ores containing these besides iron- and copper-pyrites, the richer copper-pyrites themselves, and, lastly, the intermediate products, "coarse metal," "matt," &c. These, for their metallurgical utilization, equally require a calcination evolving sulphurous acid; but the matter is very different here from what it is with a good pyrites, whether it be pure iron-pyrites or containing a few per cent. of copper. On the whole, all those ores and metallurgical products are much poorer in sulphur than ordinary good pyrites; and for this reason they are less easily calcined in such a manner as to allow of utilizing the gas, because the evolution of heat by the combustion of their own sulphur is not sufficient to maintain the process energetically. An external stimulus was required before the smelting-works would seriously attempt to utilize the sulphurous acid contained in the gas from calcining the ores; and this was, the damage and nuisance caused by the *noxious vapour* all round the works. The claims for damages, the law-suits, and the measures taken by the authorities at last made it impossible in many places for the works to go on in the old way; and although it appeared at first as if the sulphurous acid could not be condensed at all in this case, or only at a loss, practice has now succeeded in fulfilling the task in most (but not in all) cases, principally by the construction of improved burners, which will be described in the fourth Chapter.

It would undoubtedly be too much to say that the task had been solved in all its parts; the success [has mostly been only partial. In many cases where an ore could not possibly have been calcined so as to utilize the gas, mixing of it with others has been resorted to. Thus the Halsbrücke works, near Freiberg, roast galena and blende along with pyrites; and in 1870 they made 8000 tons of sulphuric acid from the gas. This properly so-called metallurgical sulphuric acid is principally made in Germany, much less in other countries.

Touching the sulphurous acid escaping as noxious vapour, Leplay (comp. Percy, 'Metallurgy,' 1862, i. p. 337) mentions that in South Wales annually 46,000 tons of sulphur escaped into the air as sulphurous acid, along with arsenic, fluorine, lead, and zinc compounds, in spite of the condensing-chambers. In fact the country round Swansea was deprived of all vegetation. At Freiberg the works in 1864 paid upwards of £2750 damages on account of their vapours in 1870, after better condensation had been effected, only £239. It should not be forgotten that sulphurous acid occurs in very large quantity, although in a much more dilute state, in all coal-smoke, and consequently in the atmosphere and the rain-water of all large towns, and that the most perfect "smoke-combustion" cannot do away with this. Much more injurious than the vapours escaping through high chimneys, which are soon diluted with air, is the smoke from brick-works, coke-ovens, and other fires which emit their smoke at a low height above the ground. Mr. Fletcher has calculated that at St. Helens the acids escaping amounted :

From fire-gases	to 800 tons per week.		
„ copper-works . . . „	380	„	„
„ glass-works . . . „	180	„	„
„ alkali-works . . . „	25	„	„

Similar calculations have been made by Mr. Hasenclever (Chem. Industrie, 1879, p. 225), who has given strong proof of the damage done by coal-smoke alone.

In Chapter IV. we shall deal with the various attempts at utilizing, or at least rendering innocuous, the acid gases given out in calcining ores, and we shall in this place only enumerate the various classes of ores or waste substances coming under the head

of causing "noxious vapours," such as might serve for the manufacture of sulphuric acid.

Zinc-blende is probably the most important of the ores in question. Enormous quantities of it are now burnt in such a way that the sulphurous fumes evolved are utilized either for the manufacture of sulphuric acid or for that of liquid sulphur dioxide. This industry is principally centred in Upper Silesia, in the Prussian Rhine province and in the adjacent districts of Belgium; it exists, however, also to a smaller extent in South Wales.

The blende used at Stolberg contains about 25 per cent. of sulphur, that at Lethmathe 32 per cent.

Iron is an injurious constituent of blende, as it causes it to give up its sulphur with much more difficulty (Minor, Chem. Zeit. 1889, p. 1602).

Copper-pyrites and mixture of this with blende, galena, &c. are roasted in several places in kilns so as to utilize the SO_2 in acid-chambers—at Chessy near Lyons, at Oker in the Harz, at Mansfield, at Swansea. At the Altenau silver-works near Clausthal in 1872, 228 tons of vitriol of 106°Tw. were made from copper-pyrites (and 314 tons from lead-matts, Wagner's 'Jahresb.' 1874, p. 276). At Freiberg the Mulden and Halsbrücke works proceed in the same way; but they only utilize the ores and products pretty rich in sulphur for vitriol-making.

At Oker (Bräuning, 'Zeitschr. f. Berg- Hütten- u. Salinenwesen im preuss. Staate,' 1877, p. 132) at present about 15,000 tons of ore per annum are used for acid-making, viz. the five following kinds :—

1. Iron-pyrites about	2500 tons.
2. Ordinary copper-pyrites	4200 „
3. Mixed ores	3350 „
4. Rich copper-ores, excluding richest in copper	750 „
5. Lead-ores containing pyrites ...	4200 „

The average composition of the ores Nos. 2 to 5 is shown in the following Table :—

	Lead ores.	Mixed ores.	Rich copper- ores.	Ordinary copper-ores.
Cu	0.55	5.06	15.64	7.90
Pb	11.79	9.52	4.88	2.17
Ag	0.016	0.016	0.017	0.01
Fe	11.86	16.26	25.32	34.93
Zn	23.86	18.99	7.90	3.71
Mn	2.18	1.75	1.64	1.08
Co+Ni	0.04	0.06	0.04	0.08
As+Sb	0.12	0.12	0.10	0.08
SiO ₂	1.06	1.53	0.87	1.70
Al ₂ O ₃	1.81	2.02	0.94	2.61
CaCO ₃	3.72	1.91	2.21	2.32
MgCO ₃	0.89	0.56	0.42	0.74
BaSO ₄	15.97	13.77	6.66	0.63
S	25.00	27.18	32.89	41.08
Total	98.866	98.746	99.547	99.04

Traces of Hg, Tl, Cd, and Se have been found both in the ores and in the products obtained therefrom.

Apart from pure pyrites, the "ordinary ores" are best adapted for vitriol-making, because they contain their sulphur mostly as FeS₂; the "mixed ores" are less favourable, on account of their galena, and the rich copper-ores on account of their large percentage of copper. Of the lead-ores only those amply permeated by pyrites are fit for vitriol-making. The sulphur in the ores worked at Oker varies from 20 to 40 per cent.; on an average it is 30 per cent.; but it must be noticed that the sulphur of the galena is altogether unavailable for vitriol-making. The case is not much better when copper-pyrites predominates, because this furnishes too poor a gas, and, moreover, decrepitates and falls to powder in roasting. If no more than 35 per cent. of copper-pyrites is mixed with iron-pyrites, it does no harm. Blende behaves in a similar way, but rather more favourably; ores containing 35 per cent. blende along with 25 per cent. pyrites yield gas quite adapted for vitriol-making.

The first sulphuric-acid works at Oker were erected in 1841; now there is there the largest production of vitriol in Germany, viz. 14 sets of chambers with a capacity of 800,000 cubic feet.

Galena is probably nowhere worked in such a way as to get out its sulphur in the shape of sulphuric acid. The purest galena contains only 13.4 per cent. of sulphur; it is transformed into lead

sulphate on roasting, and only in the strongest white heat gives off a portion of its sulphur as SO_2 ; moreover the metallurgical processes to which it is subject are of such a nature that only poor gas can be produced from it. This matter has been discussed by Bode in his 'Beiträge zur Theorie und Praxis der Schwefelsäurefabrikation,' 1872, pp. 32 & 63; his conclusion is that even mixtures of galena and pyrites cannot be roasted in kilns for vitriol-making if they contain more than 18 to 20 per cent. of galena.

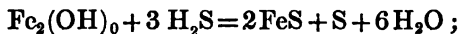
"Coarse metal" of copper-smelting is roasted for vitriol at Mansfeld. A product containing 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S, according to Bode, yields gas with $5\frac{1}{2}$ per cent. by volume of SO_2 , and at a sufficiently high temperature to work with the Glover tower. In most cases, up to the present, coarse metal cannot be roasted so as to utilize the SO_2 .

Lead-matt is used for vitriol-making—for instance, at Freiberg and in the Lower Harz; it is roasted there in large kilns of $12\frac{1}{2}$ tons capacity. The matt loses half its sulphur, and yields gas with 4 to 6 per cent. of SO_2 ; the temperature, according to Bode, is high enough for the Glover tower. In the Upper Harz, the utilization of its sulphur in metallurgy has in general not been found practicable.

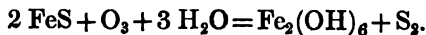
4. BY-PRODUCTS OF OTHER MANUFACTURES.

(*Spent oxide of gas-works, soda-waste, ammonia works, &c.*)

The *spent oxides* from the purification of *gas* by hydrated ferric oxide are in many places used for vitriol-making. This sulphur originally also comes from pyrites, viz. from that contained in the coal, which appears in the gas mostly as sulphuretted hydrogen. Most large works remove it, according to the patent of F. C. Hills (1857), by a mixture of hydrated iron oxide and sawdust. In this case sulphide of iron and sulphur are formed, according to the equation



and when the mass, having become inactive, is exposed to the air, it again passes over into ferric hydroxide, more sulphur being precipitated, thus,



The hydroxide thus reproduced and mixed with sulphur is again used in the purifiers, and thus regenerated about 30 or 40 times before the sulphur has accumulated therein to such an extent that the mixture does not work any more; it is then replaced by fresh oxide, and the spent ore is passed over to vitriol-makers.

Phipson states the composition of such a mass to be:—

Water.....	14 per cent.
Sulphur	60 „
Organic substance insoluble in alcohol.	3 „
Organic substance soluble in alcohol (calcium ferrocyanide and sulpho- cyanide, ammonium sulphocyanide, ammonium chloride, hydrocarbons).	1.5 „
Clay and sand	8 „
Calcium carbonate, ferric oxide, &c...	13.5 „

100

Hot water extracts the ferrocyanides and sulphocyanides, along with ammonium chloride; the solution can be evaporated to dryness, and the residue separated by alcohol into insoluble calcium ferrocyanide and soluble sulphocyanide and chloride.

According to the Analyses of Davis ('Chemical News,' xxix. 1874, p. 30), 3 samples of spent oxides contained:—

	I.	II.	III.
Sulphur	64.376	62.358	67.956
Ferric hydroxide	14.421	17.112	15.335
Insoluble	11.052	5.099	8.304
Moisture	2.079	5.387	3.900
Lime (as CaS)	2.399
Sawdust	2.470	1.776	1.002
Calcium carbonate	5.135	3.006
Ammonium sulphocyanide	2.662	1.324	1.102
Ammonium chloride	} 0.605
Ammonium cyanide.....	
Ammonium ferrocyanide	1.663
Prussian blue	trace	0.366	trace
	100.064	100.220	100.605

These samples seem to have been taken from precipitated iron hydroxide, to judge from further analyses by Davis (Chem. News, xxxvi. p. 189), in which also tarry substances are taken into account.

Residues proceeding from

	Precipitated $\text{Fe}_2(\text{OH})_6$	Bog-iron- ore.	Copperas.	Bad oxides.
Ferric hydroxide	17.74-19.36	15.96-26.42	5.04- 6.84	8.72-20.40
Sawdust	1.98- 4.72	1.14- 3.72	1.04- 3.24	2.16- 9.76
Calcium carbonate.....	0- 1.04	0- 1.73	0-	0-10.36
Ammonium sulphocyanide ...	1.99- 2.74	0.94- 1.93	1.98- 3.41	1.18- 4.72
Ammonium ferrocyanide	trace	trace- 0.21	0.27- 0.64	trace- 0.44
Tarry matters.....	0.72- 1.22	0.92- 1.14	0.72- 1.18	0.55- 1.04
Sulphur	62.44-67.18	48.76-57.44	48.76-55.74	32.42-42.16
Insoluble in dilute HCl	3.66- 5.47	9.74-11.42	7.82-12.68	12.12-20.71
Prussian blue.....	trace- 0.17	trace- 1.74	trace- 0.64
Calcium sulphate	trace- 1.43	0- 3.23
Ammonium sulphate	12.78-16.72	0- 1.14
Moisture (by difference)	4.72- 5.76	7.22-10.82	7.98- 9.22	7.49-33.41

From these analyses it can be seen, first, that it is decidedly best to extract the mass at first with water, in order to remove the ammonia compounds, which are in themselves valuable, and which, if they get into the chambers, destroy a good deal of nitre (their value is certainly greatly lessened by the sulphocyanide); secondly, that sometimes a considerable quantity of calcium carbonate is present, which may get into it at the gas-works by lime being added, on purpose or by mistake, and which, of course, retains an equivalent quantity of sulphur in the shape of gypsum. In fact a sample of the residue left after burning contained

Insoluble.....	33.386
Ferric oxide.....	52.399
Calcium sulphate	13.315
Sulphur	0.200

These impurities (which cause a loss by retaining sulphuric acid) and the sulphates present from the first (which are not available) must be allowed for in analyzing. This, according to Davis, was formerly done by extracting the sulphur by means of carbon bisulphide, evaporating the solution, and weighing off the sulphur; but as the presence of tarry matters causes an error, Davis now makes the analysis by burning the sulphur in a current of air in a combustion-tube of Bohemian glass, conducting the SO_2 formed into an absorbing apparatus filled with iodine solution, and retitrating the unaffected iodine by a solution of sodium hyposulphite (Chem. News, xxxvi. p. 190; comp. also Zulkowsky's process, p. 60).

The burning of this gas-sulphur is usually done in shelf-furnaces

similar to those used for pyrites smelts. They will be described in detail in the fourth Chapter. Already in 1861, at Barking Creek, on the Thames, 2180 tons of this material were used; but much larger quantities might have been got, since, according to A. W. Hofmann ('Report,' 1862, p. 15), even at that time at least 10,000 tons of sulphur were contained in the London gas.

In France also, at that time, the sulphur from gas-works was used on a large scale. The factory at Aubervilliers, belonging to the Society of St.-Gobain, used no other; Messrs. Seybel and Co. at Liesing, near Vienna, and Kunheim and Co. at Berlin (Wagner's Jahresb. 1864, p. 153; Hasenclever, *l. c.* p. 167) do the same.

The rational treatment of spent oxides for the purpose of obtaining ammonium salts, ferrocyanides, and sulphocyanides is described in Lunge's 'Coal-Tar and Ammonia,' 2nd edition, pp. 550, 578, 605.

The sulphur contained in *alkali-waste*, in the shape of calcium sulphide, has been frequently proposed for the manufacture of sulphuric acid, nearly always after having been first converted into *sulphuretted hydrogen*. The only successful process in this line (the Chance process of treating alkali-waste) belongs to the domain of alkali-manufacture, and cannot be treated in this volume. Only the contrivances for burning the hydrogen sulphide will be described in the fourth Chapter.

Bornträger (G. P. 15,757) proposes decomposing the yellow liquors from alkali-waste by means of ferric oxide (ground damp pyrites cinders), to filter the sulphur and ferric sulphide which is thus precipitated, and burn it after drying in ordinary shelf-burners. [Oxide of iron in this state is a very inferior reagent for removing the sulphur from yellow liquors and the like.]

The *sulphuretted hydrogen* given off in the manufacture of *sulphate of ammonia* (comp. Lunge's 'Coal-Tar and Ammonia,' p. 614) is sometimes used for the manufacture of sulphuric acid; but this is only done in a very few cases, since the H_2S is not merely diluted with a large quantity of inert gases, but is also of very unequal concentration, which usually renders the manufacture of sulphuric acid from this source an unprofitable process. The same can be said of most other cases in which H_2S is given off as a by-product.

Sulphur dioxide, formed in many manufacturing operations as a disagreeable by-product, apart from those already described, is

sometimes proposed to be converted directly or indirectly into sulphuric acid. The special cases in which this has been attempted will be treated in the next Chapter.

5. NITRATE OF SODA, NO_3Na .

$\frac{1}{2} (\text{Na}_2\text{O}) = 31$	36.47 per cent.
$\frac{1}{2} (\text{N}_2\text{O}_5) = 54$	63.53 „
85	100.00

Hardness 1.5 to 2; spec. grav. 2.09 to 2.39. In the pure state, and in large crystals, it is colourless, transparent, and brilliant as glass; in small crystals it is white and opaque. The crystals are rhombohedra with angles of $106^\circ 30'$ and $73^\circ 30'$. It has a cooling, bitter taste. Heated to a certain temperature, it melts; at a red heat it is decomposed into sodium nitrite and oxygen gas. The fusing-point is $316^\circ\text{--}319^\circ\text{C}$. (Carnelley, J. Chem. Soc. 1878, ii. p. 277). Mixed with coal, it deflagrates on heating. It attracts moisture from the air (especially if not quite free from chlorides), and readily dissolves in water, with a considerable lowering of the temperature.

1 part of sodium nitrate, according to Marx, requires for solution 1.58 part of water at -6° , 1.25 at 0° , 0.46 at $+119^\circ\text{C}$. According to Kopp, 1 part of sodium nitrate at $18^\circ.5\text{C}$. requires 1.14 of water, or 100 parts of water dissolve 87.72 parts of the salt. In the presence of sodium chloride its solubility is considerably less.

Specific Gravity of the Solutions of Sodium Nitrate at 20°C .

Parts of salt in 100 water.	Specific gravity.	Parts of salt in 100 water.	Specific gravity.
1	1.0065	10	1.0676
2	1.0131	11	1.0746
3	1.0197	12	1.0817
4	1.0264	13	1.0889
5	1.0332	14	1.0962
6	1.0399	15	1.1035
7	1.0468	16	1.1109
8	1.0537	17	1.1184
9	1.0606	18	1.1260

Parts of salt in 100 water.	Specific gravity.	Parts of salt in 100 water.	Specific gravity.
19	1·1338	35	1·2679
20	1·1418	36	1·2770
21	1·1498	37	1·2863
22	1·1578	38	1·2958
23	1·1659	39	1·3055
24	1·1740	40	1·3155
25	1·1822	41	1·3255
26	1·1904	42	1·3355
27	1·1987	43	1·3456
28	1·2070	44	1·3557
29	1·2154	45	1·3659
30	1·2239	46	1·3761
31	1·2325	47	1·3864
32	1·2412	48	1·3968
33	1·2500	49	1·4074
34	1·2589	50	1·4180

Nitrate of soda occurs in many places in small quantities; but the only large beds which supply the world with this article are situated in a region of the West Coast of South America, formerly belonging to Peru and now to Chili. This occurrence, and the industry founded thereon, have been described in various communications by Langbein (Wagner's *Jahresb.* 1871, p. 300; 1872, p. 290; 1879, p. 390); also by W. E. Billinghamurst, of whose book (written in Spanish) Darapsky gives an extract in the '*Chem. Zeit.*' xi. p. 752 (*J. Soc. Chem. Ind.* 1887, p. 545).

The nitre-beds are principally situated in the province of Tarapacá, between $68^{\circ} 15'$ and $78^{\circ} 18'$ longitude, and $19^{\circ} 12'$ and $21^{\circ} 18' 30''$ latitude; they also occur somewhat south, especially near Antofagasta and Taltal. They were discovered in 1821 by Mariano de Rivero, and have been worked since 1830. The nitre zone is situated at an altitude of 3600 feet above the sea-level.

The total area of the nitre-bearing strata is estimated by Billinghamurst at 21,212 estacas (about 150,000 acres), and the yield obtainable therefrom = 1980 millions of Spanish cwts. The nitre-bearing rock, called *caliche*, is found in layers of from 10 inches to 5 feet depth, which rarely crop out at the surface. The overlying rock, called *costra*, is 18 inches to 7 feet thick, and consists

principally of a hard conglomerate of sand, felspar, phosphates, and other minerals.

The composition of the caliche varies; it contains from 48 to 75 per cent. of sodium nitrate, 20 to 43 per cent. of sodium chloride, and varying quantities of sodium sulphate, calcium sulphate, potassium nitrate, potassium iodate, magnesium chloride, also insoluble earthy portions and organic substance (guano). It is first broken by a stone-breaking machine, and then put into the dissolvers. These are partly open square tanks, preferably, however, closed egg-shaped boilers with two man-holes—one on the top for filling in the caliche, another at the bottom for emptying the residue. The mass rests on a perforated bottom. The boilers are filled entirely with the broken rock, and half with mother liquor, and were formerly always heated by direct steam injected below the false bottom. After $1\frac{1}{2}$ to $2\frac{1}{2}$ hours the liquid, then sufficiently saturated with nitre, is run into settlers; from these it flows, after several hours, into a second settler, where, by half an hour's rest, it allows some still-suspended common salt to subside, and then runs into shallow coolers. The residue from the dissolvers, which still contains 15 to 35 per cent. of sodium nitrate, is either emptied at once or boiled once more with fresh water. The crystals, separated in the coolers after draining off the mother liquors, are spread in layers of 12 to 18 inches thickness on a large surface exposed to draught, and dried with frequent stirring. The total cost of sodium nitrate, up to its reaching European ports, in 1871, amounted to £8 18s. per ton, which leaves a good margin for profit at the average price of £12 (it has reached £16 and more).

The above-described system of dissolving by open steam has been recently abandoned for closed steam-coals or similarly-acting apparatus; at the same time air heated to 120° – 150° C. is forced through the liquid by means of injectors, in order to hasten the evaporation. This produces both stronger and purer liquors, the quantity of sodium chloride being the same in the stronger as in the weaker liquor.

The composition of the crude nitre-earth is shown by the following analyses:—

	Caliche.				Costra.
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>
Sodium nitrate	70·62	60·97	51·50	49·05	18·60
Sodium iodate	1·90	0·73
Sodium iodide	traces	traces	...
Sodium chloride	22·39	16·85	22·08	29·95	33·80
Sodium sulphate	1·80	4·56	8·99	9·02	16·64
Potassium chloride	8·55	4·57	2·44
Magnesium chloride	0·43	1·25	1·62
Magnesium sulphate	0·51	5·88
Calcium sulphate	0·87	1·31
Calcium carbonate	0·12	0·15	0·09
Silica and ferric oxide	0·90	2·80	3·00
Insoluble	0·92	4·06	6·00	3·18	20·10
Moisture	0·99	5·64
	100·00	100·00			

The analyses *a* and *b* (*a* white, *b* brown caliche) are by Machattie (Chem. News, xxxi. p. 263). They are somewhat suspicious, both on account of the total absence of potassium salts and of the extremely improbably high percentage of sodium iodate. This is all the more noticeable as Machattie at the same time states the average percentage of iodine in five samples of *mother liquor* to be = 0·56, equal to 0·873 per cent. of sodium iodate, which may be nearer the truth. The analyses *c*, *d*, and *e* are by V. L'Olivier (Compt. Rend., 26th October, 1875).

The iodine contained in the mother liquors is now recovered to a great extent, and forms one of the principal sources of this article.

Beckurts (Arch. d. Pharm. ccxxiv. p. 323; Fischer's Jahresb. 1886, p. 305) found in all descriptions of commercial nitre small quantities of chlorates and perchlorates.

R. Wagner (Jahresb. 1869, p. 248) found in commercial nitrate of soda :—

Sodium nitrate	94·03
„ nitrite	0·31
„ chloride	1·52
Potassium chloride	0·64
Sodium sulphate	0·92
„ iodate	0·29
Magnesium chloride	0·93
Boric acid	traces
Moisture	1·36

100·00

The nitrate of soda imported into England, as used by vitriol-makers, is much purer than the above sample. The English sellers mostly guarantee a maximum of 5 per cent "refraction" (that is, the total percentage of all foreign constituents, inclusive of water), frequently, however, 4 or even $3\frac{1}{2}$ per cent. refraction. English vitriol-makers would, indeed, altogether refuse nitrate containing upwards of 3 per cent. of chlorides, like that analyzed by Wagner, 1 per cent. being the maximum allowed. The muriatic acid generated from them, of course, gives, with nitric acid, free chlorine and its compounds with nitrogen oxides, and causes a loss of the latter. The average composition of nitrate for chemical works is

96 sodium nitrate (including nitrite, iodate, &c.),
0.5 chlorides (calculated as NaCl),
0.75 sulphates (calculated as Na_2SO_4),
2.75 moisture.

In the factories the value of nitrate is mostly only estimated indirectly, viz. the "refraction." 10 grams are well dried in a porcelain capsule, weighed again, dissolved, the residue (if any) is estimated, the liquid dissolved to a certain volume, and in separate portions of the liquid chlorine and sulphuric acid estimated in the usual way. The sum total of moisture, insoluble residue, sodium chloride, and sodium sulphate is called the "refraction," and it is assumed that the remainder is real sodium nitrate. This may, however, lead to very erroneous results, where, for instance, the nitre contains some potassium nitrate. A case in point has been described by me in 'Chem. Ind.' 1886, p. 369, where an error amounting to 2 per cent. was caused in this way. It is therefore preferable to make a more complete analysis in the following way:—

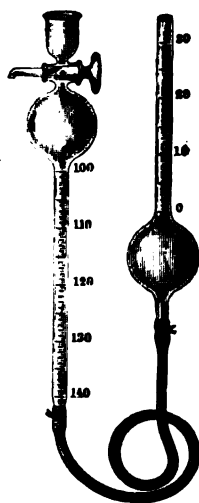
Dissolve a good-sized sample, say 20 to 30 grams, of the nitrate in twice its weight of water, employing a flask of known contents, and heating very gently. Weigh out a quantity corresponding to about 0.4 gram NaNO_3 in an ordinary weighing-glass or in a tube with stopcock, as employed for testing fuming sulphuric acid (fig. 7). Run its contents into a nitrometer, either a "bulb-nitrometer," as shown in fig. 8; or, preferably, the non-graduated nitrometer, connected with a Lunge's gas-volumeter, to be described in the next Chapter. In the latter case no observation of temperature and barometric pressure nor any reduction tables are

required. Do not rinse the weighing-tube (which would dilute the liquid too much), but weigh it back as it is. Decompose the solution within the nitrometer with a sufficient quantity of strong sulphuric acid and mercury, and measure the nitric oxide given off as will be described in the next Chapter, where also a table for reducing the readings to NaNO_3 will be given.

Fig. 7.



Fig. 8.



Of course, any other analytical method may be employed for estimating the nitre, such as heating it with silica and observing the loss of weight (not to be recommended very much), or heating with ferrous sulphate and titrating back with potassium permanganate, or boiling with a solution of ferrous chloride and observing the quantity of NO evolved (comp. next Chapter).

A deposit of *potassium nitrate* has been found near Cochabamba, in Bolivia (Sacc, Compt. Rend. xcix. p. 84). This enormous deposit consists of 60·70 per cent. potassium nitrate, 30·70 borax, a little salt and water, 8·60 organic substances. On dissolving the saline mixture in hot water and cooling, pure potassium nitrate crystallizes out. The soil on which it rests contains a large quantity of ammonium carbonate and sulphydrate, borax, and phosphates; there are also many fossil bones, which seems to indicate that this deposit was formed by the decomposition of enormous quantities of antediluvian animals. It is probable that potassium and sodium nitrate were formed at the same time, the former being drawn to the surface by capillary action, the latter being washed out by the rains and re-deposited near the coast in the universally known beds of sodium nitrate. This hypothesis concerning the formation of the nitre-beds contradicts the theory of Noellner (Wagner's Jahresb. 1868, p. 290), which is otherwise very generally accepted. According to this theory, enormous masses of seaweed have been thrown by hurricanes into the bay, at that time situated at a much lower level, the nitrogen of the seaweed, on its slow decay, occasioning the formation of caliche. In favour of this supposition are the constant occurrence of iodine in the caliche, the prevalence of westerly winds in that country, the total absence of rain, so that the nitre formed was not washed out, and the well-known gradual rising of the whole coast above the sea-level.

The total exportation of nitrate of soda from South America is shown by the following figures :—

	tons.
1830.....	935
1835.....	7,020
1840.....	11,368
1850.....	25,592
1860.....	68,512
1870.....	147,170
1871.....	180,295
1877.....	229,018
1881.....	319,000
1882.....	410,000
1883.....	530,000
1888.....	759,090
1889.....	930,000

Consumption of Nitrate of Soda.

	In Great Britain. tons.	On the Continent. tons.	In the United States. tons.
1881	65,500	165,500	55,000
1882	75,500	237,000	60,000
1883	99,000	314,000	55,000
1885	95,000	290,000	45,000
1886	106,000	320,000	60,000
1887	98,000	385,000	65,000

The importation into Germany, according to official sources, was 271,207 tons in 1888, 332,797 tons in 1889.

Importation of Nitrate of Soda into Europe from 1867 to 1887.
(Chem. Trade Journal, 1888, vol. iii. p. 386.)

Year.	England, Scotland, Ireland.	France.	Belgium.	Germany.	Holland.	Total of all Europe.
	tons.	tons.	tons.	tons.	tons.	tons.
1867	50,800	15,300	5,100	22,400	7,200	100,800
1868	45,700	17,300	4,100	23,400	8,100	98,600
1869	43,700	15,300	5,100	19,300	6,100	89,500
1870	55,900	15,800	4,800	20,300	7,100	103,700
1871	75,200	17,300	3,100	28,400	4,100	128,100
1872	87,300	32,300	4,100	49,800	4,100	177,600
1873	125,900	43,500	3,800	41,100	11,100	225,400
1874	106,200	50,500	1,900	59,400	16,400	234,400
1875	155,500	59,400	5,600	51,600	16,200	288,300
1876	161,400	59,400	6,500	59,500	18,900	305,700
1877	74,300	61,000	11,500	53,400	9,300	209,500
1878	102,700	56,300	9,200	66,800	16,500	251,500
1879	58,300	53,300	8,000	73,800	14,500	207,900
1880	48,600	13,400	9,200	49,800	18,100	139,100
1881	56,700	41,300	11,600	98,200	21,700	229,500
1882	97,600	66,600	15,500	132,000	26,400	338,100
1883	102,300	92,100	26,500	199,900	19,800	440,600
1884	104,600	1,400	57,700	224,300	31,900	419,900
1885	106,100	87,100	44,700	122,900	22,900	385,700
1886	77,200	69,300	51,300	111,200	24,600	333,600
1887	84,300	89,500	59,000	172,300	38,500	443,600

When *emptying nitrate of soda from the bags*, a certain quantity of the salt, which is always damp, remains adhering to them—

which not only causes loss, but makes them useless, and even produces a danger of fire. It is therefore well to lixiviate the bags with hot water, and to dry them. The solution is evaporated to a small bulk and crystallized. The mother liquor from this operation is always very rich in chlorides, which seems to show that the deliquescence of sodium nitrate is not a property of the pure salt, but is owing to the magnesium and calcium chloride contained in it, since the dampest salt will adhere to the bags.

6. NITRIC ACID, NO_3H .

This may also be called one of the raw materials of vitriol-making, although a manufactured product itself, in those works using it in lieu of the nitre itself.

The nitric acid proper (the monohydrate) has the equivalent 63, and may be said to contain, as formerly expressed, 85·71 nitric anhydride (N_2O_5) and 14·29 water. Its specific gravity is 1·54 at 20° , or 1·55 at 15° . It is colourless if perfectly pure; but the strongest acid of commerce is always coloured yellow, or even red, by a partial decomposition into oxygen and nitrogen tetroxide, N_2O_4 (hyponitric acid). Its boiling-point is 86°C . On boiling an acid containing a little water, at first strong acid distils over, till the boiling-point of the remainder has reached 126° , at which point the thermometer remains stationary, and an acid of constant composition for any certain pressure distils over. Exactly the same point is reached from the opposite side by distilling more dilute acids, in which case water distils over, and the remaining acid becomes more and more concentrated, till the above stationary point is reached. The acid at that point has nearly the composition $2\text{NO}_3\text{H} + 3\text{H}_2\text{O}$ (corresponding to 60 N_2O_5 and 40 H_2O) and a specific gravity of 1·42.

The following is a table of *the percentage of nitric acid for different specific gravities*, according to Kolb (Bull. Soc. Ind. de Mulhouse, 1866, p. 412):—

Degrees (Baumé).	Spec. gravity.	100 parts contain at 0° C.		100 parts contain at 15° C.	
		NO ₃ H.	N ₂ O ₅ .	NO ₃ H.	N ₂ O ₅ .
0	1.000	0.0	0.0	0.2	0.1
1	1.007	1.1	0.9	1.5	1.3
2	1.014	2.2	1.9	2.6	2.2
3	1.022	3.4	2.9	4.0	3.4
4	1.029	4.5	3.9	5.1	4.4
5	1.036	5.5	4.7	6.3	5.4
6	1.044	6.7	5.7	7.6	6.5
7	1.052	8.0	6.9	9.0	7.7
8	1.060	9.2	7.9	10.2	8.7
9	1.067	10.2	8.7	11.4	9.8
10	1.075	11.4	9.8	12.7	10.9
11	1.083	12.6	10.8	14.0	12.0
12	1.091	13.8	11.8	15.3	13.1
13	1.100	15.2	13.0	16.8	14.4
14	1.108	16.4	14.0	18.0	15.4
15	1.116	17.6	15.1	19.4	16.6
16	1.125	18.9	16.2	20.8	17.8
17	1.134	20.2	17.3	22.2	19.0
18	1.143	21.6	18.5	23.6	20.2
19	1.152	22.9	19.6	24.9	21.3
20	1.161	24.2	20.7	26.3	22.5
21	1.171	25.7	22.0	27.8	23.8
22	1.180	27.0	23.1	29.2	25.0
23	1.190	28.5	24.4	30.7	26.3
24	1.199	29.8	25.5	32.1	27.5
25	1.210	31.4	26.9	33.8	28.9
26	1.221	33.1	28.4	35.5	30.4
27	1.231	34.6	29.7	37.0	31.7
28	1.242	36.2	31.0	38.6	33.1
29	1.252	37.7	32.3	40.2	34.5
30	1.261	39.1	33.5	41.5	35.6
31	1.275	41.1	35.2	43.5	37.3
32	1.286	42.6	36.5	45.0	38.6
33	1.298	44.4	38.0	47.1	40.4
34	1.309	46.1	39.5	48.6	41.7
35	1.321	48.0	41.1	50.7	43.5
36	1.334	50.0	42.9	52.9	45.3
37	1.346	51.9	44.5	55.0	47.1
38	1.359	54.0	46.3	57.3	49.1
39	1.372	56.2	48.2	59.6	51.1
40	1.384	58.4	50.0	61.7	52.9
41	1.398	60.8	52.1	64.5	55.3
42	1.412	63.2	54.2	67.5	57.9
43	1.426	66.2	56.7	70.6	60.5
44	1.440	69.0	59.1	74.4	63.8
45	1.454	72.2	61.9	78.4	67.2
46	1.470	76.1	65.2	83.0	71.1
47	1.485	80.2	68.7	87.1	74.7
48	1.501	84.5	72.4	92.6	79.4
49	1.516	88.4	75.8	96.0	82.3
49.5	1.524	90.5	77.6	98.0	84.0
49.9	1.530	92.2	79.0	100.0	85.71
50.0	1.532	92.7	79.5		
50.5	1.541	95.0	81.4		
51.0	1.549	97.3	83.4		
51.5	1.559	100.0	85.71		

If the temperature of the acid in testing it by the hydrometer is above or below 15° C., a correction must be made for this. A detailed table for all strengths and temperatures, founded upon a series of observations, is given in Lunge and Hurter's 'Alkali-maker's Pocketbook'; we quote here only the average figures. For each degree above 15° add, or below 15° deduct, to the specific gravity observed.

0.0005	with acids from	1.000–1.080
0.0006	„ „	1.080–1.110
0.0007	„ „	1.110–1.140
0.0008	„ „	1.140–1.170
0.0009	„ „	1.170–1.220
0.0010	„ „	1.220–1.300
0.0011	„ „	1.300–1.330
0.0012	„ „	1.330–1.360
0.0013	„ „	1.360–1.390
0.0014	„ „	1.390 and upwards.

Loring Jackson and Wing, and a little later on R. Hirsch (Chem. Zeit. 1888, p. 911), have shown that the presence of *nitrous acid* (or nitrogen tetroxide) in nitric acid has a considerable influence on its specific gravity. Thus the first runnings from a distillation possessed a specific gravity = 1.62, but contained 12 per cent. by weight of HNO_2 . Hirsch assumes (without strict proof) that each per cent. of HNO_2 raises the specific gravity by 0.01. If this is correct, an acid of sp. grav. 1.44, but containing 1 per cent. HNO_2 , really contains only 99 per cent. of HNO_3 of spec. grav. 1.43. Now 100 grams of pure acid of 1.44 are = 74.4 grams HNO_3 , but 99 grams of 1.43 only = 71.0; hence the 1 per cent. of HNO_2 present makes a difference of 3.4 per cent. of HNO_3 in the real strength, compared with the apparent strength as taken from the specific-gravity tables.

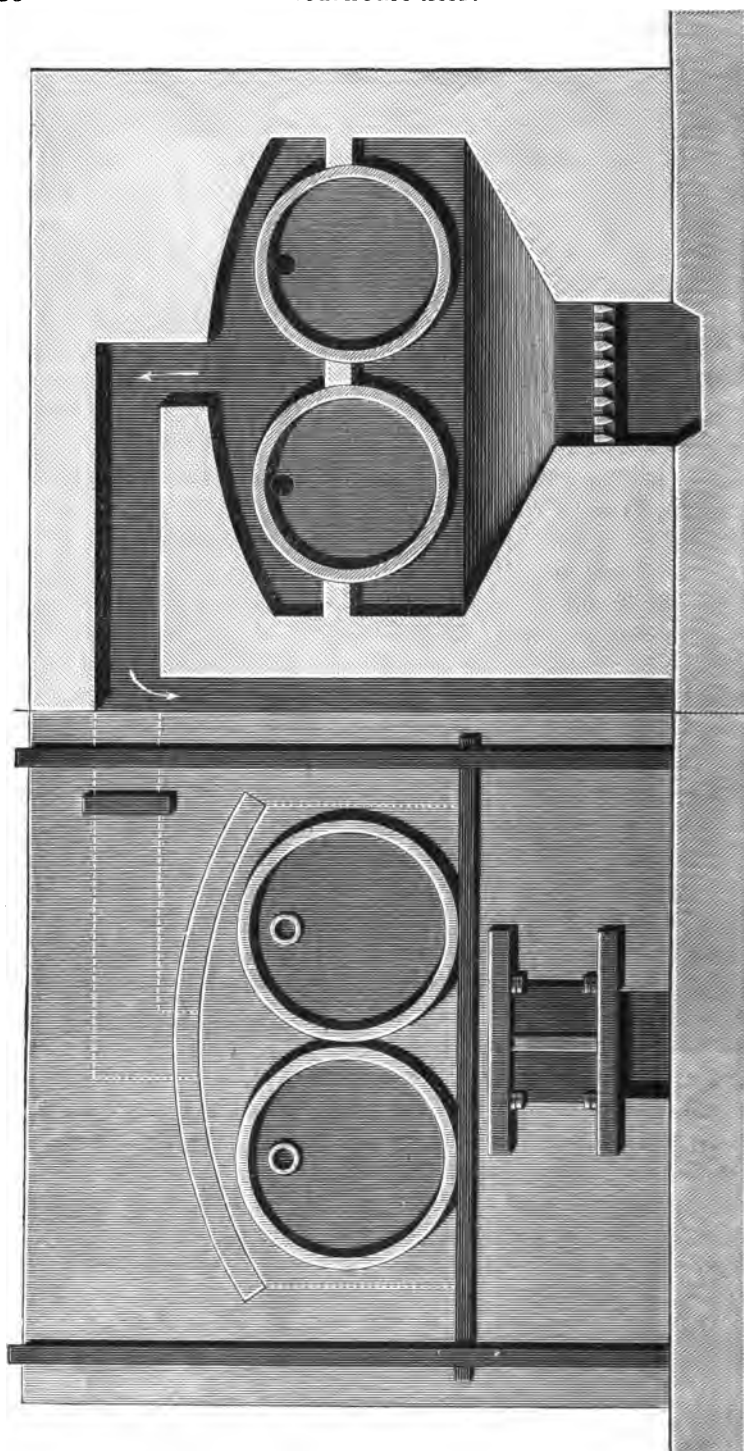
The oxidizing properties of nitric acid are well known, and cannot be described in detail here; but it should be mentioned that an acid containing the lower oxides of nitrogen, such as the "red fuming nitric acid," has even more strongly oxidizing properties than the pure acid, because this helps to explain some points in the theory of the formation of sulphuric acid, as we shall see in the respective chapter.

Nitric acid has been known since the time of Geber, in the 8th

century; and Raymundus Lullus in 1225 taught how to prepare it by distilling a mixture of clay and saltpetre. Now-a-days it is always made by distilling nitrate of soda with sulphuric acid, an excess of the latter acid beyond the theoretical quantity having to be used in practice. By the equation: $2\text{NaNO}_3 + \text{H}_2\text{SO}_4 = 2\text{HNO}_3 + \text{Na}_2\text{SO}_4$, in theory 85 parts of NaNO_3 require 49 parts of SO_4H_2 , and yield $63\text{NO}_3\text{H}$ along with $71\text{Na}_2\text{SO}_4$; this comes to the same as 57.6 parts of SO_4H_2 , or, say, 60 parts of ordinary strong oil of vitriol (with 95 per cent. of SO_4H_2) to 100 parts of 95-per-cent. nitrate. If these proportions are used, a portion of the nitric acid is always decomposed into O and N_2O_4 , and red fuming acid is obtained. This arises from the fact that the above equation is only realized at a high temperature, whilst at less elevated temperatures sodium bisulphate is formed: $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{HNO}_3 + \text{NaHSO}_4$. Moreover, the presence of strong sulphuric acid, owing to its attraction for the elements of water, has a tendency to split up some HNO_3 into H_2O and N_2O_6 , the latter compound being at once decomposed into N_2O_4 and O. To avoid the loss involved in this operation, generally more dilute nitric is produced by employing weaker sulphuric acid, say of $140^\circ\text{--}148^\circ\text{ Tw.}$, and more than the theoretical quantity of it, generally from 20 to 30 per cent. in excess of the simple equivalent. In this case the admixture of a certain quantity of sodium bisulphate makes the residue of distillation much more easily fusible, and facilitates its removal from the retorts. When the acid is made at works where salt is decomposed, even more sulphuric acid than the above is generally employed, as the excess is not lost, the residual "cylinder-cake" or "nitre-cake" being regularly mixed with the salt to be decomposed in the sulphate-pans; in this case as much sulphuric acid is saved as corresponds to the bisulphate contained in the cylinder-cake.

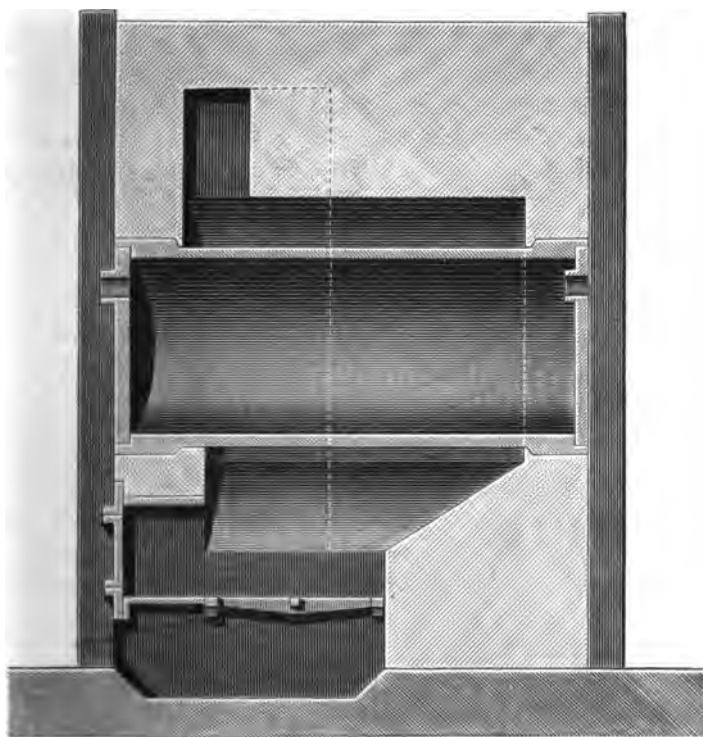
The manufacture of nitric acid takes place in very similar apparatus to those formerly used in the manufacture of hydrochloric acid, where the latter was the principal product, and which we shall describe in the second book, viz. glass retorts or cast-iron retorts. Glass retorts are very little used now on a large scale. The cast-iron retorts in most works are cylindrical, generally about 2 ft. wide, 5 ft. long, and $1\frac{1}{2}$ thick, two being heated by the same fire. Each cylinder takes a charge of $1\frac{1}{2}$ cwt. of nitre, and about the same quantity of sulphuric acid of 140° Tw.

Fig. 8 a.



Figs. 8*a* and 8*b* show the shape of retorts very frequently used, and the way of setting them, the drawings being made to the scale 1:25. The ends of the cylinders are usually exposed to the air and

Fig. 8*b*.



consist of cast-iron discs, $1\frac{1}{2}$ inch thick, cemented into the rebates cast on to the ends of the cylinder by the usual rust cement (100 iron filings, 5 flowers of sulphur, 5 sal-ammoniac), or by a mixture of this with ground fire-bricks and the like. At all events the back-end is fixed in such manner, and is provided with a pipe for taking away the vapours; the other end is made to take off and serves for charging the nitre and discharging the residue. A hole and S-shaped funnel in the man-lid allow of running in the sulphuric acid. These cylinder-ends cause a good deal of cooling, and consequently a loss of fuel, which can be avoided to a great extent if they are not made of iron but of a single stone flag each;

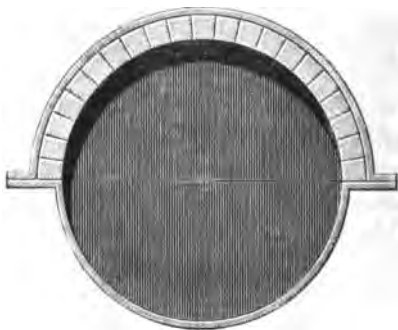
the charging end also remains fixed in this case, the nitre being charged through a small general opening in it, and the residue being run off in a liquid state through a pipe generally closed by a ground-in iron stopper. A little more sulphuric acid is employed in this case, so as to obtain a very fluid mass at the end. If the sulphuric acid is taken at 144° Tw., the receivers will contain a nitric acid of 77° to 82° Tw.; if weaker acid is desired, a little water is put into the receivers. The strongest acid, of 106° Tw., can only be made from strong vitriol and dried nitrate.

At first the cylinders are fired rather strongly; but as soon as the first receivers get warm, the fire is slackened, and during 18 hours is kept so that of eight receivers only the first five are warm to the touch. If the heat gets up too high, the contents of the retort may boil over, and far more ruddy vapours will be formed. The end of the reaction is known by the cooling of the receivers; then the fire is increased again for a little time, and at last is allowed to go down.

In regular work, there are some red vapours at first, but much less with rather weaker acid (say 135° Tw.) than with stronger acid. At the end the red or yellow vapours appear again, and last up to the finish.

The cylinders are sometimes cast so that their upper half can be protected against the attack of the acid by lining it with acid-proof bricks (see fig. 9); but according to some this does more harm

Fig. 9.

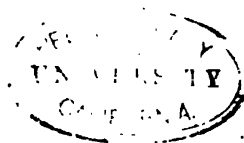
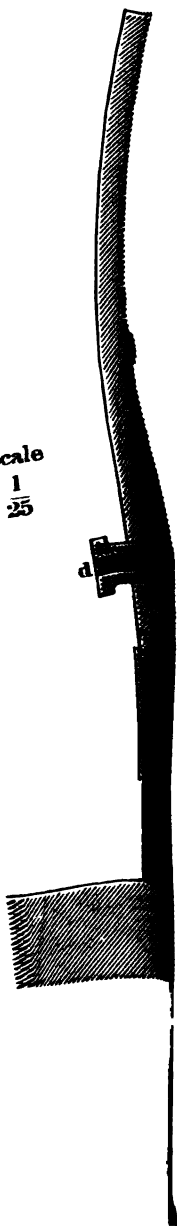


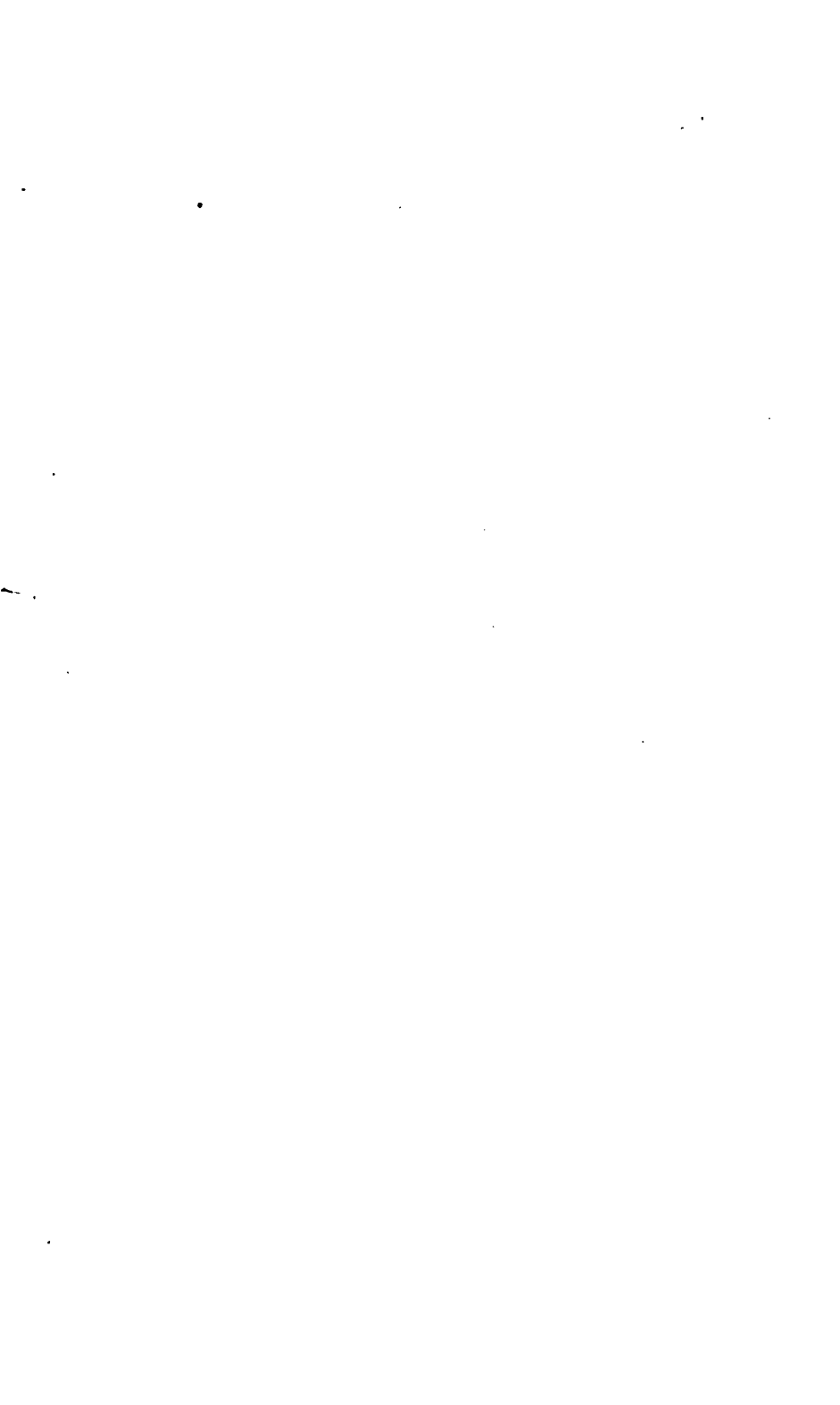
than good, as the upper part of the metal cylinder is all the less acted upon by the nitric acid the hotter it becomes.

Another form of apparatus, shown in fig. 9 *a*, is in many respects

Lange, vol. i.]

Scale
1
25





superior to the cylindrical retorts, and has been frequently introduced, especially on the Continent, in lieu of the latter, which work much more slowly and do not easily admit of making the very strongest acid. It consists of cast-iron pots of from 4 to 5 feet diameter and equal height, and a metal thickness of $1\frac{1}{4}$ to 2 inches (rather thicker at the bottom). There is a wide neck *a* at the top, closed by a lid, fastened on with a suitable cement, *e. g.* a mixture of clay and gypsum. There is a tube *b* for carrying away the gas, either coming out perpendicularly at the top, as shown here, or bending away horizontally, as in a laboratory retort; this tube ought to be lined with an earthenware tube as far as it is at all liable to cool down below the point where the metal can be acted upon by nitric acid. Another tube *c* serves for introducing the sulphuric acid; this is preferable to running it in through the neck *a*, after charging the nitre. Sometimes there is no pipe provided for running out the liquid residue, but it is better to have one, as shown at *d*, and to protect this tube against the direct action of the fire by a fire-proof covering. Where this is not provided, the liquid residue must be ladled out through *a* at the close of the operation, which is a disagreeable proceeding. The pot is set in a furnace in such manner that it is altogether surrounded by the fire, even at the top, to which access is afforded for charging by lifting off a fire-clay slab, or a metal plate filled with ashes, as shown at *e*. By this means there is a saving of fuel effected, and the equal heating of the retort causes it to stand the action of the nitric acid very well. A pot, 5 feet wide and 5 feet high, takes a charge of 9 cwt. of nitre, and requires from 16 to 18 hours to work this off, including the time for charging and emptying.

At some works they use large semicylindrical troughs of cast metal with broad flanges and a vertical rim all round, in order to cover them by a brick arch or a stone slab. At others they employ large pots with rounded bottom, lying on their side; the open end, which forms part of the front of the furnaces, being closed by a stone slab. Neither of these forms has found very much favour elsewhere.

The condensing-apparatus for nitric acid generally consists of a series of stoneware jars (Woulfe's bottles), as will be shown further on, combined in sets of seven to nine for cylinders holding $1\frac{1}{2}$ cwt. of nitre, or sixteen to twenty-four for pots holding 9 cwt. each.

According to the strength of acid intended to be made, they are

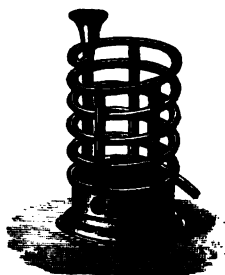
either left empty or charged with a little water, as already mentioned. Sometimes they are cooled on the outside with water; but generally this is not the case. Each of them is provided with a bottom tap for running off the condensed acid; that from the first two receivers is more impure than that of the others, as it contains a little sulphuric acid and iron carried over from the retort. The acid becomes weaker the further the receivers are from the retort. Since the receivers now and then crack with the heat, it is advisable to put them on stoneware saucers provided with a spout, for collecting the acid running out.

The cement for the temporary connexions is mostly made of clay and horsedung, or something of that kind. For luting the arms into the receivers &c. the following cement is said to serve very well:— $\frac{1}{2}$ ounce of finely powdered brimstone is shaken up with 5 lb. of hot linseed oil; 1 lb. of cut-up india-rubber scrap is added, and the whole boiled with constant stirring until it is all dissolved or converted into a homogeneous mass. After cooling, the mixture is mixed with finely ground sulphate of barytes, and worked up in an iron mortar, till it forms a tough homogeneous mass. This cement both resists the acid and preserves a certain degree of elasticity. Another cement which sets very hard consists of a mixture of asbestos and solution of silicate of soda.

Several improvements have latterly been effected in the apparatus for condensing the nitric acid. Instead of allowing the acid vapours to pass directly into the first receiver, which even with the best ware often leads to breakages, owing to the sudden change of temperature, especially with forced working, the vapours are previously cooled in different ways. Sometimes stoneware worms cooled by water are employed, of the shape of fig. 10, as supplied by Messrs. Doulton and Watts, of Lambeth, and other firms; they are very efficient, and stand changes of temperature very well. If properly manufactured they last up to two months, and far more than save their expense by the saving in receivers. These worms can be easily worked in such manner that the different fractions distilling over are separated.

A cheaper arrangement has been described by Göbel (Dingl. Journ. ccxx. p. 241). It consists in a straight glass tube, bent at


Fig. 10.



each end and lying in cold water; for each ton of nitre, $4\frac{1}{2}$ tons of cooling-water are required. This apparatus seems to be very efficient, but it requires a great deal of care in handling, and is hence not very much in use.

Much simpler, again, but not quite so efficient as cooling-worms or Göbel's apparatus, is the interposition of glass tubes with *cooling by the air only* between the retorts and the receivers. In this case

Fig. 11.



not only the cooling-water is saved, but it is possible to employ the tube in several pieces of a somewhat conical shape, loosely put together (fig. 11); only the whole must have enough fall for the condensed acids not to stop in the tubes and run out of the joints. With a length of from 10 to 13 feet (the longer the better) the cooling by air is already very efficient.

A contrivance is frequently met with for depriving the gas issuing from the last receiver of all not-condensed nitrogen oxides before they enter the chimney. This is a small Gay-Lussac's absorbing-tower (compare later on), consisting of a stack of stoneware pipes filled with coke and continually fed with sulphuric acid of 144° to 152° Tw. The gas enters at the bottom and issues at the top, and thereby gives up all its nitrous and hyponitric acids to the vitriol, which arrives at the bottom as a more or less rich "nitrous vitriol," and can be employed in the manufacture of sulphuric acid. For a ton of nitre from $3\frac{1}{2}$ to 4 cwt. of vitriol are required; and nitrogen acids corresponding to 3 to 5 per cent. of nitric acid of 1.33 spec. grav. are absorbed by the same, more or less, according to the percentage of chlorides in the nitre.

For such manufactures of nitric acid as are not in connexion with sulphuric-acid works, it is preferable to feed the coke-tower with water. If care is taken that there is always an excess of air present, not merely the last remnant of nitric acid is condensed, but the lower nitrogen oxides are likewise converted into nitric acid and thus saved.

Far preferable to coke-towers for both the just-mentioned pur-

poses are the "plate-columns," constructed by the conjunction with Mr. L. Rohrmann, and already in nitric-acid works. These will be described in detail. (in the Chapter dealing with the recovery of nitre); if we will only point out that the use of coke is irrational, it destroys nitric acid, converting it into nitrous acid and oxides. The plate-columns are made of the best fire-resisting stoneware, and, as will be seen hereafter, are constructed as to offer the most intimate possible contact to the gases and liquids. Fig. 12 shows the arrangement by L. Rohrmann (Krauschwitz near Muskau, Germany) for condensation of the last fumes, or the recovery of nitric acid and lower oxides. A B C is the stoneware shell of the tower, covered with distributing arrangement, E the plates, F the bearers, G drawing-off tap with hydraulic lute, H exit-tube for observing the condensation, K receiver, M injector for air through the neck N, in connexion with the last receiver.

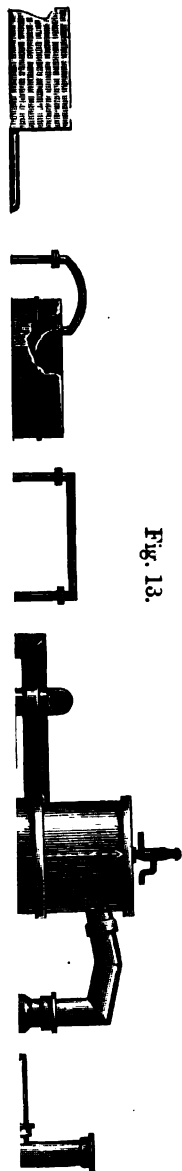
Perhaps the best process for condensing nitric acid is that invented by O. Guttman, which will be described in the Appendix. It became known to the Author too late for insertion in this work.

Figs. 13 and 14 give an elevation and top view of the condensing apparatus, as supplied by Mr. Rohrmann for use with retorts, holding 6 cwt. of nitrate of soda each, together with a retort for bleaching the acids:—*a a* receivers for impure acid, *b* carboy for the same, *c c* cooling-worms, *d* carboys for the acid, *e* collecting receiver, *f* plate-column, *g* receiver, *h* injector for bleaching, the gases being equally led into the plate-column.

The *refining* or *bleaching* of nitric acid consists in destroying the lower oxides, so that the acid is got colourless. This is done by long heating in a water-bath, which is a tedious process—much more quickly if a current of air is blown through the gently heated acid; the air along with the gas contained in the acid is conducted through a small coke-tower, or, preferably, a "plate-column" (see above), fed with water, where diluted nitric acid is contained. This refining is, of course, unnecessary if the acid is used in the manufacture of sulphuric acid.

Hirsch (G. P. 46,096) runs the impure acid through a spiral worm, placed in water of 80° C. Air is blown in at the bottom and the feed of nitric acid is regulated in such manner that it comes out at the bottom 60° C. warm and sufficiently bleached. It

Fig. 13.



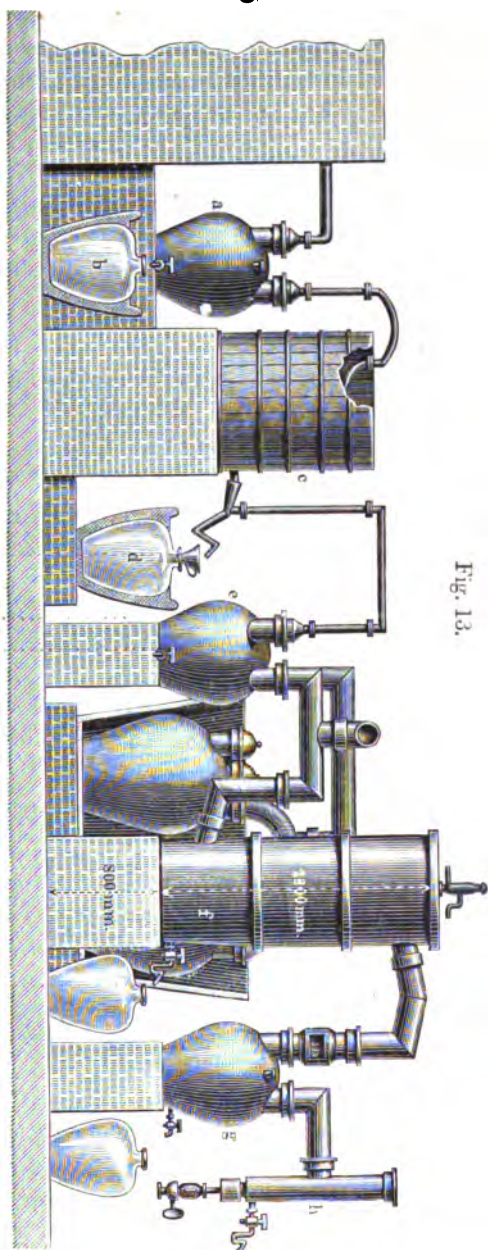


Fig. 13.

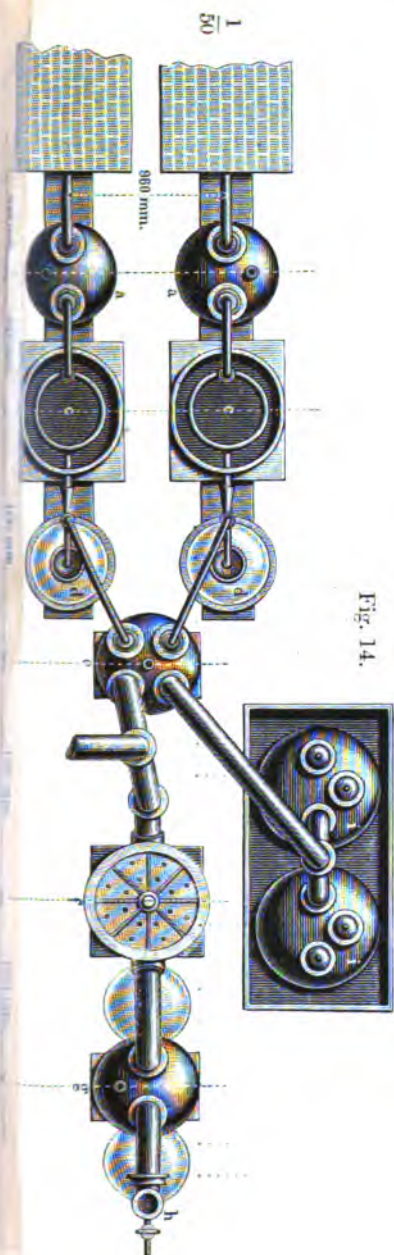


Fig. 14.

through a second worm placed in cold water, and can then be put into the carboys. The nitrous gases escaping at the top are treated in the usual manner. One worm can purify several tons of acid per diem. The same process can serve for treating the waste acid of nitroglycerine and nitrobenzene works for nitrous and nitric acids; in this case air heated to 150°C . or steam is blown in at the bottom, and the feed of acid is so regulated that it issues 140°C . warm (as comparatively pure sulphuric acid).

The *cost of manufacturing nitric acid* at a Continental factory (some years ago) has been as follows, and can be easily reduced to current English prices :—

1. *For acid of 36° Baumé (=sp. gr. 1.334 or 50 per cent. NO_3H).*

	£	s.	d.
4 charges of 4 cwt. each nitrate of soda, at 16s....	12	16	0
16 cwt. sulphuric acid 144° Tw., at 3s.	2	8	0
10 cwt. lignite (very inferior quality), at 9d.	0	7	6
2 men, at 3s.	0	6	0
Interest and writing off the plant	0	8	0
General expenses	0	1	6
Packages, &c.....	2	16	0
Yield: 21 cwt. acid at 36° Baumé	19	3	0
Cost of 1 cwt. acid at 36° Baumé.....	0	18	3

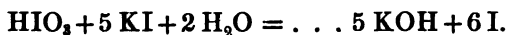
2. *For acid of 50° Baumé (=sp. gr. 1.532=93 per cent. NO_3H).*

	£	s.	d.
6 cwt. of nitrate of soda (dry), at 19s.	5	14	0
6 cwt. sulphuric acid 168° Tw., at 5s. 6d.	1	13	0
6 cwt. lignite, at 9d.	0	4	6
Wages—2 men	0	6	0
Sundries and general expenses	0	12	0
Small stores	0	11	0
Yield: 3 cwt. 2 qrs. 10 lb. acid	9	0	6
Deduct value of 5 cwt. nitre-cake	0	15	0
	8	5	6
Cost of 1 cwt. of acid 50° Baumé	2	6	0

The cost price at a French works is stated by Sorel, for 100 kil. of acid of 36° Baumé, made in large cylinders :—

	francs.
Supervision ($\frac{1}{4}$ of the foreman's wages).....	0·59
Wages of workmen	1·13
76·33 kil. nitre at 27 frs.....	20·69
83·96 kil. acid 60° B. at 2·25 frs.	1·89
36 kil. coal at 2·15 frs.....	0·77
Lighting	0·27
Repairs	2·55
General expenses	0·65
	<hr/>
	28·54
Deduct 88·54 kil. nitre-cake at 2·25 frs. ...	1·99
	<hr/>
Cost of 100 kil. nitric acid 36° B.	26·55

The *impurities contained in commercial nitric acid* may be as follows :—*Chlorine, sulphuric acid, fixed residue, iron*, all found and estimated by well-known methods. *Nitrous acid or nitrogen tetroxide* is best estimated by means of potassium permanganate, running the acid from a burette into the warm diluted solution of permanganate, as will be described in the next Chapter. (The influence of NO_2H on the specific gravity of nitric acid has been noticed above.) *Iodine* is recognized by boiling 1 c.c. in order to remove the lower nitrogen oxides and to oxidize all iodine into iodic acid, diluting with 5 c.c. previously boiled water, and adding a few drops of a solution of potassium iodide and starch, made with water free from air. A blue colour shows the presence of iodine in the original acid, according to the reaction



This test, according to Beckurts (Fischer's Jahresb. 1886, p. 305), is much more delicate than the ordinary one of reducing the iodate by zinc and extracting the iodine set free by carbon bisulphide; but Beckurts' test would, of course, lead to serious errors unless a check test was made with the iodide of potassium employed, which might itself contain some iodate.

Some vitriol-manufacturers replace part of the nitre for feeding the chambers by the *waste acid from manufacturing nitrobenzene, nitroglycerine*, and similar compounds, consisting principally of

sulphuric acid with some nitric acid. Only, as a matter of course especially in the case of acid from nitroglycerine, all drops of oil must be rigidly kept away. These acids may be used in the Glover tower, and this is indeed the best way to get rid of them, preferable to any plan for separating the nitrogen acids from the sulphuric acid (one of which—that of Hirsch—has been mentioned on p. 92), as all of these are in practice very troublesome. The waste acid from nitrobenzene, for instance, is usually about spec. grav. 1.64, and contains about 1 per cent. of nitric acid, with about $\frac{1}{4}$ per cent. of nitrobenzene.

The *fixed residue* from the manufacture of nitric acid (called “nitre-cake” or, in the workmen’s language, “sally nixon,” a corruption of *sal enixum*”) is practically a mixture of neutral and acid sodium sulphate. We treat of it in detail in Book II., and here remark only that most of it is worked up with common salt into ordinary salt-cake and hydrochloric acid; part of it is also used up directly for glass-making, but no doubt not to great advantage. Kirkman (E. P. 5703, 1889) employs it as an absorbent for ammonia, in which case a profitable utilization of Na_2SO_4 will be very difficult.

CHAPTER III.

THE PROPERTIES AND ANALYSIS OF THE TECHNICALLY
EMPLOYED OXIDES AND ACIDS OF SULPHUR.SULPHUR DIOXIDE, SO_2 .

(Sulphurous Acid; Sulphurous Anhydride.)

SULPHUR dioxide is at the ordinary temperature and pressure a colourless gas of suffocating smell, neither supporting combustion nor combustible itself directly. Even when greatly diluted with air it has a very injurious action upon vegetation (comp. further on, p. 101) and upon the animal organism.

Sulphur dioxide contains 50 per cent. by weight of sulphur and 50 per cent. oxygen. Its specific gravity has been found by various observers = 2.222 to 2.247 (air = 1); calculated from the molecular weight = 2.213. A litre of the gas at 0°C . and 760 millim. pressure weighs 2.8634 grms. Its coefficient of dilatation is not exactly equal to that of air, but rather larger, especially at lower temperatures, namely for each 1°C ., according to Amagat:—

Between 0° and 10°	0.004233
„ 10° „ 20°	0.004005
At 50°	0.003846
„ 100°	0.003757
„ 150°	0.003718
„ 200°	0.003695
„ 250°	0.003685

Its specific heat, compared to its equal weight of water, is = 0.1544; compared to its equal weight of air = 0.3414.

The density of *saturated* vapour of SO_2 (that is, in contact with liquid SO_2) at various temperatures (water of $0^\circ = 1$) is, according to Cailletet and Matthias (Compt. Rend. civ. p. 1536):—

At 7.3 C. ...	0.00624	At 100.6 C. ...	0.0786
„ 16.5 ...	0.00858	„ 123 ...	0.1340
„ 24.7 ...	0.0112	„ 130 ...	0.1607
„ 37.5 ...	0.0169	„ 135 ...	0.1888
„ 45.4 ...	0.0218	„ 144 ...	0.2195
„ 58.2 ...	0.0310	„ 152.5 ...	0.3426
„ 78.7 ...	0.0464	„ 154.9 ...	0.4017
„ 91.0 ...	0.0626	„ 156	critical point.

The heat of formation of one molecule of SO_2 (=64) from ordinary (rhombical) sulphur is =71,080 cal. (Thomsen), or 69,260 (Berthelot).

By moderate cooling sulphur dioxide can be condensed to a liquid, even without application of pressure. Liquid SO_2 is a colourless mobile fluid, of about the same refractive power as water, boiling at -10°C .; but on drawing it off at the ordinary temperature from a reservoir it remains liquid for some time, the evaporation cooling it down below its boiling-point. Its specific gravity at -20° is =1.4911, at 0° =1.4333, at $+21^\circ.7$ =1.3757; latent heat at 0° 91.2, at 10° 88.7, at 20° 84.7, at 30° 80.5.

Its vapour-tension is:—

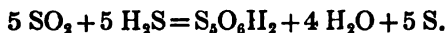
At 0°C .	= 0.53 atmosphere overpressure.
„ 10°	= 1.26 „ „
„ 20°	= 2.24 atmospheres „
„ 30°	= 3.51 „ „
„ 40°	= 5.15 „ „

The heat of the liquefaction of SO_2 is =5644 calories.

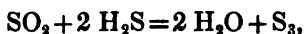
Sulphur dioxide is produced by burning brimstone, and by heating (roasting) many metallic sulphides, in the presence of air; by the action of strong mineral acids, both on its own salts, the sulphites, and on the thiosulphates and all polythionic acids; by heating sulphuric anhydride with brimstone, or by heating oil of vitrol with brimstone, coal, organic substances, or several metals; by strongly heating the vapour of sulphuric anhydride, or sulphuric acid, with simultaneous formation of oxygen and water respectively; and by igniting many sulphates, whereby the sulphuric anhydride first liberated at once splits up into sulphur dioxide and oxygen.

Thus sulphur dioxide is produced from sulphuric acid or anhydride in many ways by reductive processes. On the other

hand, the sulphur dioxide passes over, even more easily, into sulphuric acid by oxidation processes; and it is accordingly one of the most frequent and potent reducing agents. Under certain conditions, by the action of light, of the electric current, or of a very high temperature and pressure combined, the sulphur dioxide splits up into sulphur and sulphuric anhydride. In the presence of oxygen (for instance, that of atmospheric air), or of bodies easily parting with their oxygen (such as the higher oxides of nitrogen, of manganese, of lead), sulphuric acid or its salts are formed. A very important reaction is that between SO_2 and sulphuretted hydrogen, H_2S . When completely dry, the two gases do not seem to act upon each other. Even in the presence of moisture no action takes place if the temperature is above 400°C . (E. Mulder). At the ordinary temperature water and sulphur are produced, but at the same time also pentathionic acid, according to the equation



This action occurs simultaneously with the simple reaction,



one or the other of these prevailing, according to the proportion of the two gases in the mixture.

With water sulphur dioxide does not form sulphurous acid proper, SO_3H_2 , but only, under certain conditions, a solid compound with much more water (9, 11, or 15 H_2O to SO_2), which has not yet been definitively investigated. The sulphur dioxide dissolves pretty freely in water; and this solution behaves in every way as if it contained the real acid SO_3H_2 ; but constantly, even at the ordinary temperature, the dioxide (SO_2) evaporates from it. One volume of water absorbs, under 760 millim. pressure and at 0° , nearly 80 volumes SO_2 . The coefficient of absorption, according to Bunsen and Schönfeld, at temperatures ranging between 0° and 20° , is

$$79.789 - 2.6077 t + 0.029349 t^2;$$

at temperatures between 21° and 40° ,

$$75.182 - 2.1716 t + 0.01903 t^2.$$

The saturated acid contains at 0° 68.861 volumes of gaseous SO_2 ,

and has a specific gravity of 1·06091; at 10° it contains 51·383 volumes gaseous SO_2 , and has the spec. grav. 1·05472; at 20°, 86·206 volumes SO_2 , spec. grav. 1·02386. The absorbed gas does not escape on freezing—and on boiling, only completely after a long time. Alcohol absorbs a much larger volume of sulphur dioxide (at 0° and 0·76 metre pressure, 328·62 volumes SO_2).

A table, not very much deviating from the above statements, of the solubility of sulphur dioxide in water at 0·76 metre mercurial pressure at different temperatures, is given in Kopp and Will's 'Jahresberichte' for 1861, p. 54.

Anthon's Table of the Densities of Solutions of Sulphurous Acid in Water (Jahresb. 1860, p. 694).

Specific gravity.	Per cent. SO_2 .
1·005	0·95
1·009	1·90
1·013	2·86
1·016	3·82
1·020	4·77
1·023	5·72
1·027	6·68
1·031	7·63
1·036	8·52
1·046	9·54

Another table, for the temperature 15° C., is given by Scott (Pharm. Soc. J. and Trans. xi. p. 217).

Per cent. SO_2 .	Specific gravity.	Per cent. SO_2 .	Specific gravity.
0·5	1·0028	5·5	1·0302
1·0	1·0056	6·0	1·0328
1·5	1·0085	6·5	1·0353
2·0	1·0113	7·0	1·0377
2·5	1·0141	7·5	1·0401
3·0	1·0168	8·0	1·0426
3·5	1·0194	8·5	1·0450
4·0	1·0221	9·0	1·0474
4·5	1·0248	9·5	1·0497
5·0	1·0275	10·0	1·0520

Solutions of sulphurous acid in the presence of oxygen are partly converted into sulphuric acid.

According to Scott, when making sulphurous acid (mixed with CO_2) by the process mostly used, viz. that of heating oil of vitriol with charcoal, the former is best employed with 74 per cent. $\text{SO}_2 = 165^\circ \text{Tw}$. If stronger vitriol be used, a portion of it is reduced to sulphur, which may give iron sulphide with the iron of the apparatus; with weaker acid sulphuretted hydrogen is formed. In order to obtain the gas as pure as possible, the washing-water should be mixed with lead sulphate or coarsely powdered charcoal.

Sulphurous acid forms two series of salts (sulphates)—saturated or normal ones, SO_3M_2 , and acid ones, SO_3MH , isomorphous with the corresponding carbonates.

Sulphurous anhydride is absorbed by anhydrous barium oxide at 200° , better at 230° ; by strontium oxide at 230° , better at 290° ; in both cases the normal sulphite is formed. Calcium oxide forms at 400° a basic sulphite, $\text{Ca}_2\text{S}_2\text{O}_{16}$, which at 500° splits up into sulphate and sulphide. Magnesia absorbs SO_2 very slowly at 320° , and soon above this the sulphate is formed (Birnbäum & Wittich, Ber. d. d. chem. Ges. 1880, p. 651).

The reactions taking place between sulphurous acid and the oxides and acids of nitrogen will be described in a later part of this Chapter.

Injurious action of sulphurous acid.—The quantity of SO_2 which may be present in the air without being injurious to health has been stated by Hirt ('Gewerbekrankheiten,' p. 15) = 1 to 3 per cent. This is an obvious error. Ogata (Archiv f. Hygiene, 1884, p. 223) found that 0.04 per cent. SO_2 causes difficulty of breathing after a few hours; he could not take a single full breath in air containing 0.05 per cent. SO_2 . It is an acute blood-poison.

Sulphurous acid is also very injurious to vegetation, and is one of the chief constituents of the "noxious vapours" so much complained of in most manufacturing districts. It is true that these vapours contain other injurious constituents, chiefly of an acid character, viz. sulphuric anhydride, hydrogen chloride, and sometimes even the acids of nitrogen. Leaving aside the latter, and even HCl , which will be treated of in the Chapter devoted to that subject, we shall now enter upon a description of the effects produced by the ordinary "acid smoke" of metallurgical and

similar works, where SO_2 , generally also SO_3 , are the principal acids concerned.

A detailed investigation of the influence of the noxious vapours at Freiberg, where very large and numerous smelting-works are situated, on vegetation and on the health of domestic animals has been made by Freytag (abstracted in Wagner's *Jahresb.* 1873, p. 180). The sulphurous acid, sulphuric acid, arsenic, and zinc vapours of the Freiberg smelting-works under unfavourable circumstances, even with the present condensing arrangements, may damage the vegetation of the neighbourhood in the following way: at a sufficient concentration they are taken up by the leaves when covered with dew; on the evaporation of the water the organs affected are corroded and put into the same state as that which they assume when vegetation ceases. This injury can always be proved both by the eye and by chemical analysis. A "poisoning" of the soil or of the whole plant is out of the question. The assumption of an *invisible* injury done to the vegetation by the smelting-works' vapours and the awarding of damages founded thereon are unwarranted; they contradict the fundamental principles of all exact investigation and foster the desire of the unreasoning multitude to incessantly raise fresh claims for damage alleged to have been done by the works. A decrease of the nutritive value of food-plants, in cases of visible injury done to the leaves, can only occur in consequence of the loss of these leaves and the lessened ability of the plants to decompose carbonic acid and produce organic matter therefrom. Any metallic oxides or salts adhering to the leaves of food-plants may become dangerous to the animal organization by causing inflammation of the mucous membranes, and, under very unfavourable circumstances, may produce death; but this fact can always be established with certainty by *post-mortem* examination and by chemical analysis. The supposition that the "acid disease" and tuberculosis occurring in a particular neighbourhood among the cattle are produced by the noxious vapours from smelting-works is utterly unfounded and must be most decidedly contradicted. Freytag considers that air containing more than 0.003 volume per cent. of SO_2 will do injury to vegetation.

Schroeder (Wagner's *Jahresber.* 1874, p. 277) has made extensive experiments on the influence especially of sulphurous acid on vegetation, with the following principal results:—From air

containing as little as $\frac{1}{5000}$ of its volume of SO_2 , this gas is absorbed by the leaves of "leafy" (deciduous) trees and conifers; these retain it mostly, a smaller portion penetrating into the wood, the bark, and the leaf-stalks, either as such or after oxidation to sulphuric acid. Conifer-leaves absorb less sulphurous acid from the air for an equal surface of leaves than deciduous trees; the absorption takes place equally over the whole surface of the leaf, not by the stomates, and therefore has no relation to the number of the latter. A principal effect of the injurious action of sulphuric acid is its causing a check to the normal evaporation of water, the disturbance being in a direct ratio to the quantity of SO_2 ; the evaporation is mostly affected by absorption of SO_2 in sunlight, at a high temperature and in dry air. The transpiration of conifers is not visibly lowered by the same quantity of sulphurous acid as that which affects other trees (deciduous ones). The injury done by sulphurous acid is greater if the absorption takes place at the lower than if at the upper side of the leaf.

Other communications on this matter, partly contradicting those of Schroeder, have been made by Stöckhart (Wagner's 'Jahresb.' 1874, p. 228). According to his observations at Zwickau, a distance of 630 metres (= 690 yards) protects even the most sensitive vegetation against the effect of large volumes of vapours, if they escape through chimneys not less than 82 feet high. Conifers are much more sensitive than deciduous trees; the decreasing series of sensibility is—pine, pitch-pine, Scotch fir, larch, hawthorn, white beech, birch, fruit-trees, hazel-nut, horse-chestnut, oak, red beech, ash, linden, maple, poplar, alder, mountain-ash. In the parts of plants corroded by sulphurous acid, not this acid, but sulphuric acid can be found, and that to a larger extent than in the same parts of plants collected at the same time in districts free from smoke.

Schroeder and Schertel (Wagner's 'Jahresb.' 1879, p. 234) found in healthy fir-leaves 0.162 to 0.237 per cent. SO_3 ; damage was only done when the percentage rose over 0.250; the highest found was 0.592 near Freiberg, 1.33 in the Oberharz.

Other figures given by Fricke (Chem. Ind. 1887, p. 492) state the difference in the amount of SO_3 found in healthy and damaged plants as follows:—

	Healthy.	Damaged.
Beans	6.119	6.551
Buckwheat	5.110	5.880
Grass	7.105	8.336
Rye	3.684	5.610
Wheat	2.179	4.412
Cabbage	27.290	30.843
Oats	2.926	6.788
Potatoes	13.000	17.500

In most cases the differences are too slight to base any trustworthy conclusions on them. Oats, wheat, and potatoes stand the acid gases better than young meadow-plants.

Just and Heine (Chem. Industrie, 1889, p. 252) also found very varying percentages of sulphuric acid in plants alleged to be damaged by SO_2 , so that this means of tracing such damage is very unreliable.

F. Fischer, in the 230th volume of Dingler's Journal, has given a short synopsis of the researches made in this field up to 1878. A special treatise (in German) has been published on acid smoke by Hering (Cotta, 1888).

Morren (Chem. Trade Journ. ii. p. 188) shows that leaves are more sensitive to sulphurous acid than flowers. When present in a proportion of 1-80,000 in the air, the leaves of fruit-trees are visibly affected in three to five hours, and this effect seems to spread after direct action of the gas ceases. Adult leaves are usually more sensitive than young leaves. The nerves are least effected and usually remain green. Sulphurous acid dissolved in water is almost without effect on the upper surface, whilst on the lower surface each little drop causes the formation of a spot visible on both surfaces. This solution is not quickly changed into sulphuric acid; the effect of the latter is quite different from that of sulphurous acid.

Koenig (Dingler's Journal, ccxxix. p. 299) describes the appearance of trees destroyed by the vapours from roasting blende.

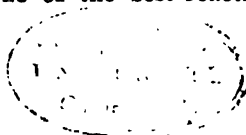
Hasenclever (Chem. Ind. 1879, p. 225) gives coloured and photolithographic illustrations of the ravages caused by acid vapours and metallic sulphates upon the leaves of plants and plantations of trees, side by side with those caused by frost, autumnal decay, fungi, drought, overgrowth of other trees, &c.,

which closely resemble the phenomena produced by the acid vapours from chemical works, and hence are frequently wrongly attributed to the latter cause. Neither is the estimation of sulphates and chlorides in the damaged leaves &c. at all a safe guide to the detection of the real cause, looking at the enormous quantity of acids sent into the air wherever coal is consumed on a large scale. At Stolberg, near Aachen, on a superficial area of 1600 acres, 220 chimneys daily emit $34\frac{1}{2}$ tons of sulphur dioxide from coal, and nearly 51 tons of SO_2 from zinc-works, glass-works, &c., the alkali-works only adding $\frac{1}{2}$ ton (more correctly 480 kilog.) of SO_2 , and $\frac{3}{4}$ ton of HCl . Hence alkali-makers ought not to be saddled with the whole, or even the chief part, of the damage observed in the neighbourhood.

An important paper on the subject in question has been published by Hamburger (Soc. Chem. Ind. 1884, p. 202). His conclusions, founded upon a large number of analyses of damaged leaves, are practically the same as Hasenclever's, namely, that undoubtedly injury is done to vegetation by the acids in the smoke, but much difficulty exists as to proving this with certainty in special cases, and at all events the SO_2 contained in ordinary coal-smoke contributes very largely to the injurious action popularly attributed to the emanations from chemical works.

Analysis of Sulphurous Acid.

Qualitative reactions of sulphurous acid.—The sense of smell is a very good means for detecting the presence of SO_2 , when other odorous acids are absent. Gaseous mixtures containing SO_2 together with such acids are best passed through an absorbent, *e. g.* sodium carbonate, with which afterwards the ordinary reactions for SO_2 are made. When passing such gaseous mixtures through a solution of potassium permanganate, or of iodine in potassium iodide, these liquids are decolorized, the iodine being reduced to HI . This last reaction may also be utilized on test-paper. On the other hand, a test-paper, soaked in a solution prepared by boiling 2 grams wheat-starch with 100 c. c. of water, and adding 0.2 gram of potassium iodate dissolved in 5 c. c. water, is turned blue by SO_2 , by the formation of free iodine. These reactions may also be utilized for recognizing the presence of SO_2 when set free from its salts by the action of sulphuric acid. One of the best reactions,



and one specially adapted for discovering SO_2 in sulphuric acid itself, is its conversion into H_2S by means of pure zinc, or, preferably, aluminium in an acid solution. The H_2S is then recognized by its reaction on lead paper, or by the purple colour produced in an ammoniacal solution of sodium nitroprusside.

A solution of a sulphate, either neutral or with addition of some sodium bicarbonate (*just* acidulated with acetic acid), when poured into a solution of zinc sulphate containing a little sodium nitroprusside, produces a red colour or precipitate, either at once or, if very little SO_2 is present, after adding some potassium ferricyanide. This reaction is not given by thiosulphates, which are, moreover, distinguished from sulphates by their giving (generally only after a little time) a precipitate of sulphur on being treated with a stronger acid. According to Reinsch, SO_2 can be detected by boiling the acid solution with a strip of clean copper, which is thereby blackened. This is caused by the formation of cupric sulphide, and the colour is not changed by heating the strip in a glass tube; whilst in case of the colour being produced by arsenic, there is a sublimate of white arsenious acid formed in the tube.

According to Schützenberger, sulphurous acid contained in a solution can be recognized by adding a very little indigo solution and agitating with a zinc rod; owing to the formation of hyposulphuric acid (Schützenberger's "hydrosulphuric" acid), HSO_2 , the blue colour will be destroyed, but will quickly reappear in contact with the air.

The *quantitative estimation* of sulphurous acid in the free state can take place either as will be described in the case of sulphates, or by titration with standard alkali. In the latter case, however, it must be noted that the point of neutrality is reached with phenolphthalein when the normal salt, Na_2SO_3 , has been formed, so that each c. c. of normal alkali (containing 0.031 NaOH) indicates 0.032 SO_2 . Of course, as is always the case with phenolphthalein, the standard alkali must be soda or potash, ammonia being useless for this purpose. But when employing methyl-orange as indicator, the point of neutrality is reached exactly at the formation of NaHSO_3 , so that each c. c. of normal alkali indicates 0.064 SO_2 . Litmus gives somewhat uncertain results, and is therefore useless as an indicator. It is thus possible to estimate free SO_2 in the presence of stronger free acids in this way: one portion of the liquid is titrated with methyl-orange, and another with phenolphthalein as

indicator; in the latter case more alkali will be used, and the difference of c. c. of normal alkali, multiplied by 0.064, shows the quantity of free SO_2 present (Lunge, J. Soc. Chem. Ind. 1883, p. 513; Thomson, Chem. News, xlvii. p. 136; Blarez, in. Compt. Rend. ciii. p. 69, adduces nothing new).

The acid sulphates are neutral to methyl-orange, which consequently allows us to estimate any SO_2 present over and above NaHSO_3 . The SO_2 present in the NaHSO_3 itself can be titrated with normal soda and phenolphthalein, each c. c. of normal alkali indicating 0.064 SO_2 . Normal sulphates, as Na_2SO_4 , can be titrated by means of methyl-orange and standard hydrochloric or sulphuric acid, the red colour appearing when NaHSO_3 has been formed, so that each c. c. of standard acid indicates 0.064 SO_2 .

Other methods of estimating SO_2 either in the free state or in its salts are based on its reducing properties. The reagents serving for this purpose are either a standard solution of iodine or one of potassium permanganate, both of which are well known and require no description here. A decinormal solution of either indicates per cubic centimetre 0.0032 gram SO_2 . The method to be recommended for testing SO_2 in burner-gas will be described when treating of that gas. Special attention must be drawn to the necessity of employing water *free from air* in estimating SO_2 . This is not necessary if the solution of the sulphate or sulphurous acid is run into the solution of iodine (Giles and Shearer, J. Soc. Chem. Ind. 1884, p. 197, and 1885, p. 303).

In many cases the quantitative estimation of sulphurous acid can take place by converting it into sulphuric acid by means of oxidizing agents: chlorine, bromine, iodine, hydrogen peroxide, &c. The sulphuric acid is then estimated in the usual way.

Sulphur dioxide in the presence of hydrogen sulphide, which gases may exist together in a state of great dilution by inert gases (as in the exit-gases from "Claus kilns"), can be estimated by passing the gases through a solution of I in KI, followed by one of caustic soda. The iodine oxidizes H_2S into $\text{H}_2\text{O} + \text{S}$, and SO_2 into H_2SO_4 ; hence the acidity of the solution is not affected by H_2S , merely by SO_2 . On the other hand, each c. c. of decinormal iodine indicates 0.0032 gram of sulphur in either case, so that the difference between the iodometrical and the alkalimetical test gives the H_2S present. The addition of a tube with caustic soda is necessary, because the gaseous current carries away some iodine

which is retained in the soda; the latter, before titrating the iodine solution back, is added to it, care being taken that the solution is acid before performing the titration (details in my paper, J. Soc. Chem. Ind., November 1890).

Applications of Sulphurous Acid.

The greatest quantity of SO_2 is produced for the manufacture of sulphuric acid. Next to this in importance comes its use for the manufacture of wood-pulp, mostly in the state of calcium bisulphate (or a solution of CaSO_3 in an excess of sulphurous acid). One of the oldest uses of sulphurous acid, in the shape of burning sulphur, is as a disinfecting and antiseptic agent. For the former purpose it is not so much valued now as formerly, since it has been shown that many of the disease-germs resist the action of SO_2 for a long time. The antiseptic function of SO_2 comes into play in the fumigation of wine-casks, in the arresting of the fermentation of wort, in the manufacture of glue (where it acts also as a bleaching agent), and in many other cases.

In the textile industries sulphurous acid is largely used as a bleaching agent, especially for wool, silk, straw, &c. It is not quite certain in which way it acts in this case, possibly by forming a compound with the colouring-matters contained in the fibres. Formerly it was generally assumed that the SO_2 in bleaching acted as a reducing agent, which indeed must be true in some, although probably not in all cases. The reducing functions of SO_2 are utilized in chemical and metallurgical operations in too many cases to be enumerated here.

SULPHURIC ANHYDRIDE, SO_3 (Sulphur Trioxide),

consists of 40 per cent. by weight of sulphur, and 60 per cent. of oxygen. According to Marignac and Schultz-Sellack, it exists in two different modifications, a liquid and a solid one. The liquid, α -anhydride melts at $+16^\circ \text{C.}$, and begins to boil at $+35^\circ$ (according to Schultz-Sellack, at 46°). Spec. grav. at $13^\circ = 1.9546$, at $+20^\circ$ (melted) $= 1.97$. In the melted state it is less oily than oil of vitriol, and, if pure, colourless, but usually coloured brown by dust. When kept for some time at the ordinary temperature (below 25°) it is changed into the *solid*, β -anhydride, whose melting-point is

rated very differently, from 50° to 100° C. Probably it begins to melt at 50° , and gradually passes over into the α -modification; it slowly evaporates even at the ordinary temperature. It forms fine, feathery, asbestos-like, white needles. The β -anhydride is perhaps a polymer of the α -modification. According to R. Weber, however (Poggendorff's Ann. cliv. p. 313), the sulphur trioxide, obtained absolutely pure and free from water by his method, is at the summer temperature a very mobile, colourless liquid, which, on gradually cooling, solidifies to long, transparent, prismatic crystals similar to nitrate of potash, quite different from the white, opaque crystals of the ordinary anhydride containing a little water. These crystals melt at $14^{\circ}8$ C., and boil at $46^{\circ}2$. Under certain circumstances the anhydride can, like many other bodies, be cooled much below its proper melting-point without solidifying, but then solidifies suddenly. After a twelvemonth it still shows the same composition and the same melting-point as that which has been freshly prepared. Weber accordingly rejects the assumption of two different modifications, and ascribes the phenomena of this kind observed by others, especially the formation of the modification resembling asbestos, to a minute residue of water.

The heat of formation of one molecule, = 80 parts by weight of SO_3 , from S and O_2 is = 103,230 cal. (Thomsen); from $\text{SO}_2 + \text{O}$ = 34,400 cal. in the solid state, or = 22,600 cal. in the gaseous state (Berthelot). The heat of vaporizing 1 mol. SO_3 is = 11,800 cal.; that produced by dissolving 1 mol. SO_3 in a large quantity of water = 39,170 cal. (Thomsen).

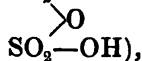
In moist air sulphuric anhydride at once forms dense white fumes; with water it hisses like a red-hot iron. Many organic substances are at once charred by it. In the complete absence of water it does not redden litmus. It gives several compounds with sulphur, whose colour, with the quantity of sulphur decreasing, changes from brown to green and blue. In the blue modification Weber has proved the presence of the sesquioxide, S_2O_3 . With sulphur dioxide there seems to exist a distinct compound, $\text{SO}_2 + 2\text{SO}_3$. With water SO_3 at once combines to form sulphuric acid (SO_3H_2) and its different hydrates. It is, however, not easy to condense the sulphuric anhydride often produced in considerable quantity in technical processes *completely*, even with a large quantity of water and manifold contact; and quite special precautions have to be taken for this purpose.

The anhydride SO_3 , when conducted through a red-hot tube splits up into SO_2 and O , but is reformed from these gases at a somewhat lower heat, especially in the presence of platinum and several metallic oxides. We shall see the technical application of this reaction later on.

For scientific purposes the sulphuric anhydride is made by gently heating fuming oil of vitriol, or by igniting sodium pyrosulphate ($\text{Na}_2\text{S}_2\text{O}_7$). Its production in a perfectly pure state is described by Weber (*l.c.*). Until quite recently it has not been used for technical purposes, owing partly to the costliness of its production, partly to the supposed difficulty of handling and keeping it. Recently, however, its production has been made so much cheaper that certain branches of manufacture already employ it advantageously. Its application has turned out to be a very simple affair, as it can be sent out in drums made of tinned iron. Its handling is certainly unpleasant, since the contact of the skin with liquid anhydride, or even just liquefying by absorbing moisture, causes very malignant and slowly-curing burns. Its production on a manufacturing scale will be described in Chapter XV.

PYROSULPHURIC ACID, $\text{S}_2\text{O}_7\text{H}_2$

(Structural formula, $\text{SO}_3\text{—OH}$



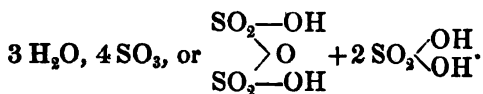
contains as constituents 89.89 parts of sulphuric anhydride and 10.11 of water, or equal molecules of hydrate and anhydride. A transparent crystalline mass, melting at 35°C ., it decomposes at moderate heat into anhydride (SO_3) and oil of vitriol (SO_4H_2).

Pyrosulphuric acid is contained in the *Nordhausen fuming acid* of trade, which often consists altogether of it, and then bears the trade name, "solid oleum." Pyrosulphuric acid can also be easily obtained from the ordinary liquid fuming Nordhausen acid by cooling below 0° . Lastly, it can be made by carefully mixing anhydride with a small quantity of oil of vitriol. Weber (*l.c.*) obtained an intermediate hydrate, $\text{H}_2\text{SO}_4 \cdot 3 \text{SO}_3$, corresponding to 94.69 per cent. of SO_3 .

Pyrosulphuric acid forms salts, of which those of the alkaline metals are the best-known and most important. Thus sodium

pyrosulphate ($S_2O_7Na_2$) is formed by fusing acid sodium sulphate (SO_3NaH) at incipient red-heat (below $400^\circ C.$). At a full red-heat it splits up further into neutral sulphate (SO_4Na_2) and sulphuric anhydride (SO_3); this reaction is sometimes utilized for producing the latter compound. In contact with water, the pyrosulphates are gradually retransformed into acid sulphates.

A compound with 14.44 per cent. H_2O can also be obtained, which crystallizes in thin transparent prisms, fumes in the air, and melts at $26^\circ C.$ Formula—



The *Nordhausen oil of vitriol*, the manufacture of which will be described in the 15th Chapter, is a viscous oil, representing a mixture of pyrosulphuric acid with sulphuric hydrate in varying proportions, and therefore solidifying at very different temperatures. It fumes in the air, and boils at 30° to $40^\circ C.$, giving out vapours of anhydride, whilst monohydrate remains behind. Water transforms it at once into ordinary oil of vitriol, with strong evolution of heat. It is often coloured brown by organic substances, and, according to its mode of preparation, contains many other impurities, such as iron, sodium, calcium, aluminium, &c. (as sulphates), sulphurous acid, selenium, organic matters, &c. When the receivers used in its preparation are charged with ordinary strong vitriol, the impurities of the latter will likewise pass into the fuming acid.

SULPHURIC ACID, H_2SO_4 .

Natural Occurrence.

Free sulphuric acid is found very exceptionally in nature, whilst some sulphates, especially that of calcium, occur in enormous quantities.

In the free state sulphuric acid has been found especially in a few springs of volcanic origin, and in the rivers fed by those springs. One of the best known cases of this kind is the Rio Vinagre in Mexico, which contains 0.111 per cent. free sulphuric acid (calculated as SO_3), and 0.091 per cent. free HCl ; it daily carries into the sea 38 tons, according to others even 69 tons of

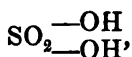
both acids. Many other similar cases have been discovered in various parts of the world (comp. the first edition of this work, i. p. 17). Other cases again occur from the oxidation of sulphur ores, the acid being expelled by heat from the sulphates generated at first.

Miners are only too familiar with the occurrence of free acid in pit-waters from similar causes, by the corrosion of metal pumps and steam-boilers; even the leather of the valves thereby becomes brittle, and the wooden parts are charred. In the case of volcanoes, sulphuric acid is formed by the oxidation of the sulphuretted hydrogen and the sulphurous acid from the fumaroles and solfataras.

Even in the animal kingdom free sulphuric acid has been found, viz. in the salivary glands of several mollusks, especially of *Dolium galea*, which contain 2·47 per cent. free sulphuric acid and 0·4 per cent. of free hydrochloric acid (Boedeker and Troschel; De Luca and Panceri).

Monohydrated Sulphuric Acid, H₂SO₄.

The proper sulphuric hydrate, commonly called as above, has the rational formula:—



and may be considered as containing 81·63 per cent. SO₃ and 18·37 per cent. water. It is a limpid, colourless, oily liquid. Its specific gravity at 0° is 1·853; at 15° (compared with water of 4°): 1·8384 (Lunge and Naef), 1·8378 (Schertel), 1·8372 (Marignac, F. Kohlrausch, Mendelejeff)*. The specific gravity changes to the extent of ±0·001 for each degree Centigrade. Both the addition of very little SO₃ and that of very little water raises the specific gravity (see below). The pure monohydrate solidifies at about 0° and forms large, plate-shaped crystals which melt at +10°·5; they remain liquid a good deal below that temperature, but solidify on agitation, or even better when a fragment of the solid hydrate is introduced. The acid begins to boil at 290°, but the boiling-point rises up to 338° (Marignac). This shows that it does not distil unchanged: in fact a mixture of hydrated acid, anhydride, and water passes over (see below). This dissociation begins much earlier; the

* Comp. Berl. Ber. 1884, pp. 1748, 2536, 2711.

pure monohydrate fumes, that is gives off SO_3 , very slightly even at the ordinary summer temperature, distinctly at 30° or 40° . Accordingly it cannot be obtained by boiling down or distilling dilute acid, but by adding an exactly sufficient quantity of anhydride to the strongest acid obtainable by concentration, or by cooling such acid below 0° and several times recrystallizing the monohydrate in the same way. The latter process has been made commercially available by the Author for the manufacture of monohydratic sulphuric acid, which since that time is no longer a laboratory product, but has become an important article of commerce.

The *vapour* of sulphuric acid consists for the most part, or even entirely (according to the temperature), not of molecules of SO_4H_2 , but of isolated molecules of SO_3 and H_2O ; theory would give to SO_4H_2 (2 vols.) a vapour-density of 3.862, for separated molecules of SO_3 and H_2O (4 vols.) a vapour-density of 1.6931, whilst Deville and Troost at 440° found it actually = 1.74. The dissociation is therefore as good as complete in the state of vapour; and this assumption agrees very well with our present notions about the state of vapour (Dittmar, Chem. News, xx. p. 258).

Formation of Sulphuric Acid.—It has been asserted that sulphuric acid is formed in damp flowers of sulphur, even at the ordinary temperature; this is certainly the case on heating sulphur with water to 200°C ., or by the electric current. Sulphur is easily oxidized to sulphuric acid by chlorine, hypochlorous acid, nitric acid, aqua regia, &c. It is produced, along with sulphurous acid and sulphur, from tri-, tetra-, and pentathionic acids—from the former by merely heating, from all three by the action of chlorine or bromine, or even on the prolonged action of stronger acids, which set the thionic acids free; also thiosulphates yield sulphuric acid under the action of chlorine. All these decompositions have to be kept in view in alkali-making.

Mostly sulphuric acid is formed from sulphurous acid. The aqueous solution of the latter is gradually transformed into sulphuric acid by the action of the air alone, and it is so transformed at once by chlorine, bromine, iodine, hypochlorous acid, nitric acid, and several metallic salts, such as manganic sulphate, mercurous nitrate, &c. Sulphur dioxide and oxygen conducted through a red-hot tube containing platinum, platinized asbestos, ferric

oxide, &c., in the presence of water yield sulphuric acid, in its absence sulphuric anhydride. Far more important than all these cases is the formation of sulphuric acid from sulphurous acid by atmospheric oxygen, nitrous acid acting as the carrier of the latter. This is the foundation of the manufacture of sulphuric acid, and will be explained in detail later on.

The heat of formation of 98 parts SO_4H_2 is:—

	Liquid.	In diluted solutions.
From SO_2 , O, H_2O	54,400	72,000 calories
„ S, O_3 , H_2O	124,000	141,000 „
„ S, O_4 , H_2	193,000	210,000 „

The heat of neutralization of 1 mol. (98 parts) H_2SO_4 by 2 mols. (80 parts) NaOH in the presence of 400 mols. of water is given by Thomsen = 31,380 cals. Pickering (Journ. Chem. Soc. 1889, p. 323) states it only = 28,197 cals.

Sulphuric acid containing water.—The strongest oil of vitriol obtainable by boiling-down ordinary pure sulphuric acid contains a quantity of water which is not stated alike by different observers (Marignac, Pfaundler, Roscoe, Dittmar, Lunge and Naef, &c.). The statements differ from 97·86 to 98·99 per cent. of SO_4H_2 ; it is at all events very nearly $98\frac{1}{2}$ per cent. This *distilled sulphuric acid* solidifies a little below 0° ; but it also shows the phenomenon of superfusion in a very high degree. It boils at 338° (Marignac), or 315° to 317° C. (Pfaundler and Pölt). Usually Marignac's statement is considered the most reliable; the acid of Pfaundler and Pölt probably contained a little more water. The boiling takes place quietly under a stronger pressure than the ordinary one, but at a lower pressure with violent bumping, which can be avoided by putting in platinum wire or scraps, according to Dittmar even better by conducting a slow current of air through it during the boiling (see Chapter X., purification of sulphuric acid).

The ordinary "*rectified oil of vitriol*" contains always more water than that obtainable by the highest degree of concentration or distillation. Exceptionally 98 per cent. is made for commercial purposes; the usual rectified O.V., formerly called 170° Twaddell, now more accurately 168° Twaddell, varies in strength from 96 down to 93 or even 92 per cent. of real monohydrate. This variation is partly caused by the fact that at the

higher degree of concentration a slight difference in specific gravity corresponds to a great difference in percentage; partly by the fact that the specific gravity of commercial acids, owing to the presence of impurities, is always higher than that of the pure acid; but apart from this, the correctness of ordinary hydrometers is rarely of a very high order. Still, it must be conceded that in England at least there is a possibility of making the hydrometers all alike, the basis of Twaddell's system being a plain and unmistakable one, as every degree is equal to a difference of 0.005. But matters are far worse on the continent and in America, where Baumé's hydrometer is almost universally used; unfortunately the degrees of this instrument, as stated by various authorities, answer to very different specific gravities, and those of the instruments found in trade often show even far greater deviations. The only rational hydrometer on Baumé's system which rests on a mathematical basis, and therefore should be always obtainable in a uniform manner, is that graduated according to the formula

$$d = \frac{144.3}{144.3 - n},$$

where d means any special density (specific gravity), and n the degree of the scale corresponding to it. (The mathematical deduction of this formula is given in the first edition of this work, pp. 20 and 21). This scale is also generally accepted in Germany and France now. It is the only one in which the degree 66, which is that everywhere accepted for rectified O.V., comes near the real specific gravity of pure sulphuric acid of 96 per cent., or commercial acid of 94 to 95 per cent, namely 1.840. Unfortunately, apart from various other scales, Gerlach's scale is also sometimes used, although this is far lower than the "rational" scale, and, to make the confusion still greater, the American manufacturers have recently adopted again another scale, based on the formula

$$n = 145 - \frac{145}{d}.$$

In order to clear the way as far as possible, we give herewith a table showing the value of a degree Baumé according to the rational scale, to Gerlach's, and to the American scale (the last is copied from A. H. Elliott, 'Chem. Trade Journal,' vol. ii. p. 183).

Comparison of Baumé's Hydrometers with the Specific Gravities.

Degrees.	Ratona Hydrometer, 144.3 $d = \frac{144.3}{144.3 - n}$	Baumé's Hydrometer (Gerlach).	American Hydro- meter.	Degrees.	Rational Hydrometer, 144.3 $d = \frac{144.3}{144.3 - n}$	Baumé's Hydrometer (Gerlach).	Ameri- can Hydro- meter
1	1.007	1.0068	1.005	36	1.332	1.3250	1.334
2	1.014	1.0138	1.011	37	1.345	1.3370	1.342
3	1.022	1.0208	1.023	38	1.357	1.3494	1.359
4	1.029	1.0280	1.029	39	1.370	1.3619	1.362
5	1.037	1.0353	1.036	40	1.383	1.3746	1.366
6	1.045	1.0426	1.043	41	1.397	1.3876	1.365
7	1.052	1.0501	1.050	42	1.410	1.4009	1.413
8	1.060	1.0576	1.057	43	1.424	1.4143	1.422
9	1.067	1.0653	1.064	44	1.438	1.4281	1.441
10	1.075	1.0731	1.071	45	1.453	1.4421	1.451
11	1.083	1.0810	1.086	46	1.468	1.4564	1.470
12	1.091	1.0890	1.093	47	1.483	1.4710	1.480
13	1.100	1.0972	1.100	48	1.498	1.4860	1.500
14	1.108	1.1054	1.107	49	1.514	1.5012	1.510
15	1.116	1.1138	1.114	50	1.530	1.5167	1.531
16	1.125	1.1224	1.122	51	1.540	1.5325	1.541
17	1.134	1.1310	1.136	52	1.563	1.5487	1.561
18	1.142	1.1398	1.143	53	1.580	1.5652	1.573
19	1.152	1.1487	1.150	54	1.597	1.5820	1.594
20	1.162	1.1578	1.158	55	1.615	1.5993	1.616
21	1.171	1.1670	1.172	56	1.634	1.6169	1.627
22	1.180	1.1763	1.179	57	1.652	1.6349	1.650
23	1.190	1.1858	1.186	58	1.671	1.6533	1.661
24	1.200	1.1955	1.201	59	1.691	1.6721	1.683
25	1.210	1.2053	1.208	60	1.711	1.6914	1.705
26	1.220	1.2153	1.216	61	1.732	1.7111	1.725
27	1.231	1.2254	1.231	62	1.753	1.7313	1.747
28	1.241	1.2357	1.238	63	1.774	1.7520	1.767
29	1.252	1.2462	1.254	64	1.796	1.7731	1.789
30	1.263	1.2569	1.262	65	1.819	1.7948	1.814
31	1.274	1.2677	1.269	66	1.842	1.8171	1.836
32	1.285	1.2788	1.285				
33	1.297	1.2901	1.293				
34	1.308	1.3015	1.309				
35	1.320	1.3131	1.317				

Comparison between the Degrees of Twaddell's Hydrometer and Specific Gravities.

Degrees, Tw.	Specific Gravity.	Degrees, Tw.	Specific Gravity.	Degrees, Tw.	Specific Gravity.	Degrees, Tw.	Specific Gravity.
1	1.005	44	1.220	87	1.435	130	1.650
2	1.010	45	1.225	88	1.440	131	1.655
3	1.015	46	1.230	89	1.445	132	1.660
4	1.020	47	1.235	90	1.450	133	1.665
5	1.025	48	1.240	91	1.455	134	1.670
6	1.030	49	1.245	92	1.460	135	1.675
7	1.035	50	1.250	93	1.465	136	1.680
8	1.040	51	1.255	94	1.470	137	1.685
9	1.045	52	1.260	95	1.475	138	1.690
10	1.050	53	1.265	96	1.480	139	1.695
11	1.055	54	1.270	97	1.485	140	1.700
12	1.060	55	1.275	98	1.490	141	1.705
13	1.065	56	1.280	99	1.495	142	1.710
14	1.070	57	1.285	100	1.500	143	1.715
15	1.075	58	1.290	101	1.505	144	1.720
16	1.080	59	1.295	102	1.510	145	1.725
17	1.085	60	1.300	103	1.515	146	1.730
18	1.090	61	1.305	104	1.520	147	1.735
19	1.095	62	1.310	105	1.525	148	1.740
20	1.100	63	1.315	106	1.530	49	1.745
21	1.105	64	1.320	107	1.535	150	1.750
22	1.110	65	1.325	108	1.540	151	1.755
23	1.115	66	1.330	109	1.545	152	1.760
24	1.120	67	1.335	110	1.550	153	1.765
25	1.125	68	1.340	111	1.555	54	1.770
26	1.130	69	1.345	112	1.560	155	1.775
27	1.135	70	1.350	113	1.565	156	1.780
28	1.140	71	1.355	114	1.570	157	1.785
29	1.145	72	1.360	115	1.575	158	1.790
30	1.150	73	1.365	116	1.580	159	1.795
31	1.155	74	1.370	117	1.585	160	1.800
32	1.160	75	1.375	118	1.590	161	1.805
33	1.165	76	1.380	119	1.595	162	1.810
34	1.170	77	1.385	120	1.600	163	1.815
35	1.175	78	1.390	121	1.605	164	1.820
36	1.180	79	1.395	122	1.610	165	1.825
37	1.185	80	1.400	123	1.615	166	1.830
38	1.190	81	1.405	124	1.620	167	1.835
39	1.195	82	1.410	125	1.625	168	1.840
40	1.200	83	1.415	126	1.630	169	1.845
41	1.205	84	1.420	127	1.635	170	1.850
42	1.210	85	1.425	128	1.640		
43	1.215	86	1.430	129	1.645		

The percentage of *mixtures of sulphuric acid and water* is in the great majority of cases tested by the hydrometer only, and many tables have been constructed for this purpose. It would be very desirable, as Hasenclever points out (Hofmann's Report, i. 181), if all sulphuric-acid-makers used the same reduction-tables for their calculations; for in the statements on the yield of acid, and in many other cases, frequently different tables are used; so that the working results of different factories are not always comparable with each other. This very clearly appears from the following comparative Table:—

Degrees (Baumé)	Spec. Grav. (Kolb).	Percentage of SO_4H_2 in the Vitriol according to							
		Vauque- lin.	D'Arcet.	Tables of different works.				Bineau.	Kolb.
10	1.075	11.73	...	11.5	11.40	...	10.98	11.0	10.8
20	1.162	24.01	...	23.3	23.46	...	21.97	22.4	22.2
30	1.263	36.52	...	36.9	36.60	...	35.93	34.9	34.7
40	1.383	50.41	...	51.6	51.49	...	49.94	38.4	48.3
50	1.530	66.54	66.45	66.9	66.17	63.8	63.92	62.7	62.5
60	1.711	84.22	82.34	83.3	82.80	79.4	79.90	78.0	78.1
66	1.842	100.00	100.00	100.0	100.00	94.0	97.87	100.0	100.0

The totally incorrect tables of Vauquelin and D'Arcet are used, up to the present time, exclusively in the south of France.

We shall here not take any notice of those old tables, nor of those of Ure, Dalton, &c., and we refer to our first edition as to the more modern and reliable tables of Bineau and Kolb. In this place we give only the most modern and accurate results, viz., those of Lunge and Isler (Zsch. f. angew. Ch. 1890, p. 129) for the strengths up to 142°Tw. ; and those of Lunge and Naef (Chem. Ind. 1883, p. 37)*.

* Since the above was written, a very extended study of the specific gravities of sulphuric-acid solutions has been published by Pickering (Journ. of the Chem. Soc. vol. lvii. p. 64 *et seq.*). The reasons why I do not see any occasion for accepting Pickering's figures in lieu of my own are stated in the Journal of the Society of Chemical Industry, Nov. 1890.

Specific Gravities of Sulphuric Acid according to Lunge & Inter and Lunge & Naef.

Spec. Grav. at 15° in the vacuum).	Degree Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent. :—				1 litre of chemically pure acid contains kilograms of :—			
			SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.	SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.
1.000	0	0	0.07	0.09	0.12	0.14	0.001	0.001	0.001	0.001
1.005	0.7	1	0.68	0.83	1.06	1.33	0.007	0.008	0.011	0.013
1.010	1.4	2	1.28	1.57	2.01	2.51	0.013	0.016	0.020	0.025
1.015	2.1	3	1.88	2.30	2.95	3.68	0.019	0.023	0.030	0.037
1.020	2.7	4	2.47	3.03	3.88	4.85	0.025	0.031	0.040	0.050
1.025	3.4	5	3.07	3.76	4.82	6.02	0.032	0.039	0.049	0.062
1.030	4.1	6	3.67	4.49	5.78	7.18	0.038	0.046	0.059	0.074
1.035	4.7	7	4.27	5.23	6.73	8.37	0.044	0.054	0.070	0.087
1.040	5.4	8	4.87	5.96	7.64	9.54	0.051	0.062	0.079	0.099
1.045	6.0	9	5.45	6.67	8.55	10.67	0.057	0.071	0.089	0.112
1.050	6.7	10	6.02	7.37	9.44	11.79	0.063	0.077	0.099	0.124
1.055	7.4	11	6.59	8.07	10.34	12.91	0.070	0.085	0.109	0.136
1.060	8.0	12	7.16	8.77	11.24	14.03	0.076	0.093	0.119	0.149
1.065	8.7	13	7.73	9.47	12.14	15.15	0.082	0.102	0.129	0.161
1.070	9.4	14	8.32	10.19	13.05	16.30	0.089	0.109	0.140	0.174
1.075	10.0	15	8.90	10.90	13.96	17.44	0.096	0.117	0.150	0.188
1.080	10.6	16	9.47	11.60	14.87	18.58	0.103	0.125	0.161	0.201
1.085	11.2	17	10.04	12.30	15.76	19.68	0.109	0.133	0.171	0.213
1.090	11.9	18	10.60	12.99	16.65	20.78	0.116	0.142	0.181	0.227
1.095	12.4	19	11.16	13.67	17.52	21.87	0.122	0.150	0.192	0.240
1.100	13.0	20	11.71	14.35	18.39	22.96	0.129	0.158	0.202	0.253
1.105	13.6	21	12.27	15.03	19.26	24.05	0.136	0.166	0.212	0.265
1.110	14.2	22	12.82	15.71	20.13	25.14	0.143	0.175	0.223	0.279
1.115	14.9	23	13.36	16.36	20.96	26.18	0.149	0.183	0.234	0.292
1.120	15.4	24	13.89	17.01	21.80	27.22	0.156	0.191	0.245	0.305
1.125	16.0	25	14.42	17.66	22.63	28.26	0.163	0.199	0.255	0.318
1.130	16.5	26	14.95	18.31	23.47	29.30	0.169	0.207	0.265	0.331

Specific Gravities of Sulphuric Acid (continued).

Spec. Grav. at 4° (in the vacuum).	Degree Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent.:—				1 litre of chemically pure acid contains kilograms of :—			
			SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.	SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.
1.135	17.1	27	15.48	18.98	24.29	30.34	0.176	0.215	0.276	0.344
1.140	17.7	28	16.01	19.61	25.13	31.38	0.183	0.223	0.287	0.358
1.145	18.3	29	16.54	20.26	25.96	32.43	0.190	0.231	0.297	0.371
1.150	18.8	30	17.07	20.91	26.79	33.46	0.196	0.239	0.308	0.385
1.155	19.3	31	17.59	21.56	27.61	34.48	0.203	0.248	0.319	0.398
1.160	19.8	32	18.11	22.19	28.43	35.50	0.210	0.257	0.330	0.412
1.165	20.3	33	18.64	22.83	29.25	36.53	0.217	0.266	0.341	0.426
1.170	20.9	34	19.16	23.47	30.07	37.55	0.224	0.275	0.352	0.439
1.175	21.4	35	19.69	24.12	30.90	38.59	0.231	0.283	0.363	0.453
1.180	22.0	36	20.21	24.76	31.73	39.62	0.238	0.292	0.374	0.467
1.185	22.5	37	20.73	25.40	32.55	40.64	0.246	0.301	0.386	0.481
1.190	23.0	38	21.26	26.04	33.37	41.66	0.253	0.310	0.397	0.495
1.195	23.5	39	21.78	26.68	34.19	42.69	0.260	0.319	0.409	0.511
1.200	24.0	40	22.30	27.32	35.01	43.71	0.268	0.328	0.420	0.525
1.205	24.5	41	22.82	27.95	35.83	44.72	0.275	0.337	0.432	0.539
1.210	25.0	42	23.33	28.58	36.66	45.73	0.282	0.346	0.444	0.553
1.215	25.5	43	23.84	29.21	37.45	46.74	0.290	0.355	0.455	0.568
1.220	26.0	44	24.36	29.84	38.23	47.74	0.297	0.364	0.466	0.583
1.225	26.4	45	24.88	30.48	39.05	48.77	0.305	0.373	0.478	0.598
1.230	26.9	46	25.39	31.11	39.86	49.78	0.312	0.382	0.490	0.612
1.235	27.4	47	25.88	31.70	40.61	50.72	0.320	0.391	0.502	0.626
1.240	27.9	48	26.35	32.28	41.37	51.65	0.327	0.400	0.513	0.640
1.245	28.4	49	26.83	32.86	42.11	52.58	0.334	0.409	0.524	0.655
1.250	28.8	50	27.29	33.43	42.84	53.49	0.341	0.418	0.535	0.669
1.255	29.3	51	27.76	34.00	43.57	54.40	0.348	0.426	0.547	0.683
1.260	29.7	52	28.22	34.57	44.30	55.31	0.356	0.435	0.558	0.697
1.265	30.2	53	28.69	35.14	45.03	56.22	0.363	0.444	0.570	0.711
1.270	30.6	54	29.15	35.71	45.76	57.14	0.370	0.454	0.581	0.725
1.275	31.1	55	29.62	36.29	46.50	58.06	0.377	0.462	0.593	0.740
1.280	31.5	56	30.10	36.87	47.24	58.99	0.385	0.472	0.605	0.755

1.285	57	32.0	30.57	37.45	47.90	59.92	0.393	0.481	0.617	0.770
1.290	58	32.4	31.04	38.03	48.73	60.85	0.403	0.490	0.629	0.785
1.295	59	32.8	31.62	38.61	49.47	61.78	0.408	0.500	0.641	0.800
1.300	60	33.3	31.99	39.19	50.21	62.70	0.416	0.510	0.654	0.816
1.305	61	33.7	32.46	39.77	50.96	63.63	0.424	0.519	0.665	0.830
1.310	62	34.2	32.94	40.35	51.71	64.56	0.432	0.529	0.677	0.845
1.315	63	34.6	33.41	40.83	52.45	65.45	0.439	0.538	0.689	0.860
1.320	64	35.0	33.88	41.50	53.18	66.40	0.447	0.548	0.702	0.876
1.325	65	35.4	34.35	42.08	53.92	67.33	0.455	0.557	0.714	0.892
1.330	66	35.8	34.80	42.66	54.67	68.26	0.462	0.567	0.727	0.908
1.335	67	36.2	35.27	43.20	55.36	69.12	0.471	0.576	0.739	0.923
1.340	68	36.6	35.71	43.74	56.05	69.98	0.479	0.586	0.751	0.938
1.345	69	37.0	36.14	44.28	56.74	70.85	0.486	0.596	0.763	0.953
1.350	70	37.4	36.58	44.82	57.43	71.71	0.494	0.605	0.775	0.968
1.355	71	37.8	37.02	45.35	58.11	72.56	0.502	0.614	0.787	0.983
1.360	72	38.2	37.45	45.88	58.79	73.41	0.509	0.624	0.800	0.998
1.365	73	38.6	37.89	46.41	59.48	74.26	0.517	0.633	0.812	1.014
1.370	74	39.0	38.32	46.94	60.13	75.10	0.525	0.643	0.824	1.029
1.375	75	39.4	38.75	47.47	60.83	75.95	0.533	0.653	0.836	1.044
1.380	76	39.8	39.18	48.00	61.51	76.80	0.541	0.662	0.849	1.060
1.385	77	40.1	39.62	48.53	62.19	77.65	0.549	0.672	0.861	1.075
1.390	78	40.5	40.05	49.06	62.87	78.50	0.557	0.682	0.873	1.091
1.395	79	40.8	40.48	49.59	63.55	79.34	0.564	0.692	0.886	1.107
1.400	80	41.2	40.91	50.11	64.21	80.18	0.573	0.702	0.899	1.123
1.405	81	41.6	41.33	50.63	64.88	81.01	0.581	0.711	0.912	1.138
1.410	82	42.0	41.76	51.15	65.55	81.86	0.589	0.721	0.924	1.154
1.415	83	42.3	42.17	51.66	66.21	82.66	0.597	0.730	0.937	1.170
1.420	84	42.7	42.57	52.15	66.92	83.44	0.604	0.740	0.949	1.185
1.425	85	43.1	42.96	52.63	67.44	84.21	0.612	0.750	0.961	1.200
1.430	86	43.4	43.36	53.11	68.06	84.98	0.620	0.759	0.973	1.215
1.435	87	43.8	43.75	53.59	68.68	85.74	0.628	0.769	0.986	1.230
1.440	88	44.1	44.14	54.07	69.29	86.51	0.636	0.779	0.998	1.246
1.445	89	44.4	44.53	54.55	69.90	87.28	0.643	0.789	1.010	1.261
1.450	90	44.8	44.92	55.03	70.52	88.05	0.651	0.798	1.023	1.277
1.455	91	45.1	45.31	55.50	71.12	88.80	0.659	0.808	1.035	1.292
1.460	92	45.4	45.69	55.97	71.72	89.55	0.667	0.817	1.047	1.307
1.465	93	45.8	46.07	56.43	72.31	90.29	0.675	0.827	1.059	1.323
1.470	94	46.1	46.45	56.90	72.91	91.04	0.683	0.837	1.072	1.338
1.475	95	46.4	46.83	57.37	73.51	91.79	0.691	0.846	1.084	1.354

Specific Gravities of Sulphuric Acid (continued).

Spec. Grav. at $\frac{15^{\circ}}{4^{\circ}}$ (in the vacuum).	Degree Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent. :—				1 litre of chemically pure acid contains kilograms of :—			
			SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.	SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.
1.480	46.8	96	47.21	57.83	74.10	92.53	0.699	0.856	1.087	1.370
1.485	47.1	97	47.57	58.28	74.68	93.25	0.707	0.865	1.109	1.385
1.490	47.4	98	47.95	58.74	75.27	93.98	0.715	0.876	1.122	1.400
1.495	47.8	99	48.34	59.22	75.88	94.75	0.723	0.885	1.134	1.417
1.500	48.1	100	48.73	59.70	76.50	95.52	0.731	0.896	1.147	1.433
1.405	48.4	101	49.12	60.18	77.12	96.29	0.739	0.906	1.160	1.449
1.510	48.7	102	49.51	60.65	77.72	97.04	0.746	0.916	1.174	1.465
1.515	49.0	103	49.89	61.12	78.32	97.79	0.756	0.926	1.187	1.481
1.520	49.4	104	50.28	61.59	78.93	98.54	0.764	0.936	1.199	1.498
1.525	49.7	105	50.66	62.06	79.52	99.30	0.773	0.946	1.213	1.514
1.530	50.0	106	51.04	62.53	80.13	100.05	0.781	0.957	1.226	1.531
1.535	50.3	107	51.43	63.00	80.73	100.80	0.789	0.967	1.239	1.547
1.540	50.6	108	51.78	63.43	81.28	101.49	0.797	0.977	1.252	1.563
1.545	50.9	109	52.12	63.85	81.81	102.16	0.805	0.987	1.264	1.579
1.550	51.2	110	52.46	64.26	82.34	102.82	0.813	0.996	1.276	1.593
1.555	51.5	111	52.79	64.67	82.87	103.47	0.821	1.006	1.289	1.609
1.560	51.8	112	53.12	65.06	83.39	104.13	0.829	1.015	1.301	1.624
1.565	52.1	113	53.46	65.49	83.92	104.78	0.837	1.025	1.313	1.640
1.570	52.4	114	53.80	65.90	84.44	105.44	0.845	1.035	1.325	1.656
1.575	52.7	115	54.13	66.30	84.95	106.08	0.853	1.044	1.338	1.671
1.580	53.0	116	54.46	66.71	85.48	106.73	0.861	1.054	1.351	1.686
1.585	53.3	117	54.80	67.13	86.03	107.41	0.869	1.064	1.364	1.702
1.590	53.6	118	55.18	67.59	86.62	108.14	0.877	1.075	1.377	1.719
1.595	53.9	119	55.55	68.05	87.20	108.88	0.886	1.085	1.391	1.737
1.600	54.1	120	55.93	68.51	87.79	109.62	0.895	1.096	1.405	1.754
1.605	54.4	121	56.30	68.97	88.38	110.36	0.904	1.107	1.419	1.772
1.610	54.7	122	56.68	69.43	88.97	111.09	0.913	1.118	1.432	1.789
1.615	55.0	123	57.05	69.89	89.56	111.82	0.921	1.128	1.446	1.806
1.620	55.2	124	57.40	70.32	90.11	112.51	0.930	1.139	1.460	1.823
1.625	55.5	125	57.75	70.74	90.65	113.18	0.938	1.150	1.473	1.840

1 4284	507 4	1 285	646 03	71 10	91 19	113 46	0 917	1 146	1 257
1 4285	507 5	1 287	646 03	71 37	91 71	114 51	0 917	1 146	1 257
1 4286	507 6	1 288	646 03	71 53	92 25	115 14	0 917	1 146	1 257
1 4287	507 7	1 289	646 03	72 30	92 77	115 44	0 917	1 146	1 257
1 4288	507 8	1 290	646 03	72 40	93 29	115 51	0 917	1 146	1 257
1 4289	507 9	1 291	646 03	73 23	93 81	117 17	0 917	1 146	1 257
1 4290	508 0	1 292	646 03	73 44	94 36	117 52	0 917	1 146	1 257
1 4291	508 1	1 293	646 03	74 07	94 92	118 51	0 917	1 146	1 257
1 4292	508 2	1 294	646 03	74 51	95 48	119 23	0 917	1 146	1 257
1 4293	508 3	1 295	646 03	74 97	96 07	119 05	0 917	1 146	1 257
1 4294	508 4	1 296	646 03	75 42	96 85	120 67	0 917	1 146	1 257
1 4295	508 5	1 297	646 03	75 56	97 21	121 38	0 917	1 146	1 257
1 4296	508 6	1 298	646 03	76 30	97 77	123 06	0 917	1 146	1 257
1 4297	508 7	1 299	646 03	76 73	98 32	123 77	0 917	1 146	1 257
1 4298	508 8	1 300	646 03	77 17	98 89	125 47	0 917	1 146	1 257
1 4299	508 9	1 301	646 03	77 60	99 44	124 16	0 917	1 146	1 257
1 4300	509 0	1 302	646 03	78 04	100 00	124 86	0 917	1 146	1 257
1 4301	509 1	1 303	646 03	78 48	100 56	125 57	0 917	1 146	1 257
1 4302	509 2	1 304	646 03	78 92	101 13	126 27	0 917	1 146	1 257
1 4303	509 3	1 305	646 03	79 36	101 69	126 98	0 917	1 146	1 257
1 4304	509 4	1 306	646 03	79 80	102 25	127 68	0 917	1 146	1 257
1 4305	509 5	1 307	646 03	80 24	102 82	128 38	0 917	1 146	1 257
1 4306	509 6	1 308	646 03	80 68	103 38	129 09	0 917	1 146	1 257
1 4307	509 7	1 309	646 03	81 12	103 95	129 79	0 917	1 146	1 257
1 4308	509 8	1 310	646 03	81 56	104 52	130 49	0 917	1 146	1 257
1 4309	509 9	1 311	646 03	82 00	105 08	131 20	0 917	1 146	1 257
1 4310	510 0	1 312	646 03	82 44	105 64	131 90	0 917	1 146	1 257
1 4311	510 1	1 313	646 03	82 88	106 21	132 61	0 917	1 146	1 257
1 4312	510 2	1 314	646 03	83 32	106 77	133 31	0 917	1 146	1 257
1 4313	510 3	1 315	646 03	83 90	107 51	134 24	0 917	1 146	1 257
1 4314	510 4	1 316	646 03	84 50	108 27	135 20	0 917	1 146	1 257
1 4315	510 5	1 317	646 03	85 10	109 05	136 16	0 917	1 146	1 257
1 4316	510 6	1 318	646 03	85 70	109 82	137 14	0 917	1 146	1 257
1 4317	510 7	1 319	646 03	86 30	110 58	138 08	0 917	1 146	1 257
1 4318	510 8	1 320	646 03	86 90	111 35	139 06	0 917	1 146	1 257
1 4319	510 9	1 321	646 03	87 50	112 25	140 16	0 917	1 146	1 257
1 4320	511 0	1 322	646 03	88 30	113 15	141 28	0 917	1 146	1 257
1 4321	511 1	1 323	646 03	89 05	114 11	142 48	0 917	1 146	1 257
1 4322	511 2	1 324	646 03	90 06	115 33	144 08	0 917	1 146	1 257
1 4323	511 3	1 325	646 03	90 56	116 55	145 68	0 917	1 146	1 257
1 4324	511 4	1 326	646 03	91 57	117 77	147 28	0 917	1 146	1 257
1 4325	511 5	1 327	646 03	92 58	118 99	148 88	0 917	1 146	1 257
1 4326	511 6	1 328	646 03	93 59	120 21	150 48	0 917	1 146	1 257
1 4327	511 7	1 329	646 03	94 60	121 43	152 08	0 917	1 146	1 257
1 4328	511 8	1 330	646 03	95 61	122 65	153 68	0 917	1 146	1 257
1 4329	511 9	1 331	646 03	96 62	123 87	155 28	0 917	1 146	1 257
1 4330	512 0	1 332	646 03	97 63	125 09	156 88	0 917	1 146	1 257
1 4331	512 1	1 333	646 03	98 64	126 31	158 48	0 917	1 146	1 257
1 4332	512 2	1 334	646 03	99 65	127 53	160 08	0 917	1 146	1 257
1 4333	512 3	1 335	646 03	100 66	128 75	161 68	0 917	1 146	1 257
1 4334	512 4	1 336	646 03	101 67	129 97	163 28	0 917	1 146	1 257
1 4335	512 5	1 337	646 03	102 68	131 19	164 88	0 917	1 146	1 257
1 4336	512 6	1 338	646 03	103 69	132 41	166 48	0 917	1 146	1 257
1 4337	512 7	1 339	646 03	104 70	133 63	168 08	0 917	1 146	1 257
1 4338	512 8	1 340	646 03	105 71	134 85	169 68	0 917	1 146	1 257
1 4339	512 9	1 341	646 03	106 72	136 07	171 28	0 917	1 146	1 257
1 4340	513 0	1 342	646 03	107 73	137 29	172 88	0 917	1 146	1 257
1 4341	513 1	1 343	646 03	108 74	138 51	174 48	0 917	1 146	1 257
1 4342	513 2	1 344	646 03	109 75	139 73	176 08	0 917	1 146	1 257
1 4343	513 3	1 345	646 03	110 76	140 95	177 68	0 917	1 146	1 257
1 4344	513 4	1 346	646 03	111 77	142 17	179 28	0 917	1 146	1 257
1 4345	513 5	1 347	646 03	112 78	143 39	180 88	0 917	1 146	1 257
1 4346	513 6	1 348	646 03	113 79	144 61	182 48	0 917	1 146	1 257
1 4347	513 7	1 349	646 03	114 80	145 83	184 08	0 917	1 146	1 257
1 4348	513 8	1 350	646 03	115 81	147 05	185 68	0 917	1 146	1 257
1 4349	513 9	1 351	646 03	116 82	148 27	187 28	0 917	1 146	1 257
1 4350	514 0	1 352	646 03	117 83	149 49	188 88	0 917	1 146	1 257
1 4351	514 1	1 353	646 03	118 84	150 71	190 48	0 917	1 146	1 257
1 4352	514 2	1 354	646 03	119 85	151 93	192 08	0 917	1 146	1 257
1 4353	514 3	1 355	646 03	120 86	153 15	193 68	0 917	1 146	1 257
1 4354	514 4	1 356	646 03	121 87	154 37	195 28	0 917	1 146	1 257
1 4355	514 5	1 357	646 03	122 88	155 59	196 88	0 917	1 146	1 257
1 4356	514 6	1 358	646 03	123 89	156 81	198 48	0 917	1 146	1 257
1 4357	514 7	1 359	646 03	124 90	158 03	200 08	0 917	1 146	1 257
1 4358	514 8	1 360	646 03	125 91	159 25	201 68	0 917	1 146	1 257
1 4359	514 9	1 361	646 03	126 92	160 47	203 28	0 917	1 146	1 257
1 4360	515 0	1 362	646 03	127 93	161 69	204 88	0 917	1 146	1 257
1 4361	515 1	1 363	646 03	128 94	162 91	206 48	0 917	1 146	1 257
1 4362	515 2	1 364	646 03	129 95	164 13	208 08	0 917	1 146	1 257
1 4363	515 3	1 365	646 03	130 96	165 35	209 68	0 917	1 146	1 257
1 4364	515 4	1 366	646 03	131 97	166 57	211 28	0 917	1 146	1 257
1 4365	515 5	1 367	646 03	132 98	167 79	212 88	0 917	1 146	1 257
1 4366	515 6	1 368	646 03	133 99	169 01	214 48	0 917	1 146	1 257
1 4367	515 7	1 369	646 03	135 00	170 23	216 08	0 917	1 146	1 257
1 4368	515 8	1 370	646 03	136 01	171 45	217 68	0 917	1 146	1 257
1 4369	515 9	1 371	646 03	137 02	172 67	219 28	0 917	1 146	1 257
1 4370	516 0	1 372	646 03	138 03	173 89	220 88	0 917	1 146	1 257
1 4371	516 1	1 373	646 03	139 04	175 11	222 48	0 917	1 146	1 257
1 4372	516 2	1 374	646 03	140 05	176 33	224 08	0 917	1 146	1 257
1 4373	516 3	1 375	646 03	141 06	177 55	225 68	0 917	1 146	1 257
1 4374	516 4	1 376	646 03	142 07	178 77	227 28	0 917	1 146	1 257
1 4375	516 5	1 377	646 03	143 08	179 99	228 88	0 917	1 146	1 257
1 4376	516 6	1 378	646 03	144 09	181 21	230 48	0 917	1 146	1 257
1 4377	516 7	1 379	646 03	145 10	182 43	232 08	0 917	1 146	1 257
1 4378	516 8	1 380	646 03	146 11	183 65	233 68	0 917	1 146	1 257
1 4379	516 9	1 381	646 03	147 12	184 87	235 28	0 917	1 146	1 257
1 4380	517 0	1 382	646 03	148 13	186 09	236 88	0 917	1 146	1 257
1 4381	517 1	1 383	646 03	149 14	187 31	238 48	0 917	1 146	1 257
1 4382	517 2	1 384	646 03	150 15	188 53	240 08	0 917	1 146	1 257
1 4383	517 3	1 385	646 03	151 16	189 75	241 68	0 917	1 146	1 257
1 4384	517 4	1 386	646 03	152 17	190 97	243 28	0 917	1 146	1 257
1 4385	517 5	1 387	646 03	153 18	192 19	244 88	0 917	1 146	1 257
1 4386	517 6	1 388	646 03	154 19	193 41	246 48	0 917	1 146	1 257
1 4387	517 7	1 389	646 03	155 20	194 63	248 08	0 917	1 146	1 257
1 4388	517 8	1 390	646 03	156 21	195 85	249 68	0 917	1 146	1 257
1 4389	517 9	1 391	646 03	157 22	197 07	251 28	0 917	1 146	1 257
1 4390	518 0	1 392	646 03	158 23	198 29	252 88	0 917	1 146	1 257
1 4391	518 1	1 393	646 03	159 24	199 51	254 48	0 917	1 146	1 257
1 4392	518 2	1 394	646 03	160 25	200 73	256 08	0 917	1 146	1 257
1 4393	518 3	1 395	646 03	161 26	201 95	257 68	0 917	1 146	1 257
1 4394	518 4	1 396	646 03	162 27	203 17	259 28	0 917	1 146	1 257
1 4395	518 5	1 397	646 03	163 28	204 39	260 88	0 917	1 146	1 257
1 4396	518 6	1 398	646 03	164 29	205 61	262 48	0 917	1 146	1 257
1 4397	518 7	1 399	646 03	165 30	206 83	264 08	0 917	1 146	1 257
1 4398	518 8</								

Specific Gravities of Sulphuric Acid (continued).

Spec. Grav. at 15° in the vacuum).	Degree Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent. :—				1 litre of chemically pure acid contains kilograms of :—			
			SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.	SO ₃ .	H ₂ SO ₄ .	acid of 142° Tw.	acid of 106° Tw.
1821	73.63	90.20	115.59	144.32	1.941	1.643	2.104	2.628
1822	65.1	...	73.80	90.40	115.84	144.64	1.945	1.647	2.110	2.635
1823	73.96	90.60	116.10	144.96	1.948	1.651	2.116	2.643
1824	65.2	...	74.12	90.80	116.35	145.28	1.952	1.656	2.122	2.650
1825	...	165	74.29	91.00	116.61	145.60	1.956	1.661	2.128	2.657
1826	65.3	...	74.49	91.25	116.93	146.00	1.960	1.666	2.135	2.664
1827	74.69	91.50	117.25	146.40	1.964	1.671	2.142	2.675
1828	65.4	...	74.86	91.70	117.51	146.72	1.968	1.676	2.148	2.682
1829	75.03	91.90	117.76	147.04	1.972	1.681	2.154	2.689
1830	...	166	75.19	92.10	118.02	147.36	1.976	1.685	2.159	2.696
1831	65.5	...	75.35	92.30	118.27	147.68	1.980	1.690	2.165	2.704
1832	75.53	92.52	118.56	148.03	1.984	1.695	2.172	2.711
1833	65.6	...	75.72	92.75	118.85	148.40	1.988	1.700	2.178	2.720
1834	75.96	93.05	119.23	148.86	1.993	1.706	2.186	2.730
1835	65.7	...	76.27	93.43	119.72	149.49	1.400	1.718	2.196	2.743
1836	...	167	76.57	93.80	120.19	150.08	1.406	1.722	2.207	2.755
1837	76.90	94.20	120.71	150.72	1.412	1.730	2.217	2.769
1838	65.8	...	77.23	94.60	121.22	151.36	1.419	1.739	2.228	2.782
1839	77.55	95.00	121.74	152.00	1.426	1.748	2.239	2.795
1840	65.9	...	78.04	95.60	122.61	152.96	1.436	1.759	2.254	2.814
18405	...	168	78.33	95.95	122.96	153.52	1.441	1.765	2.262	2.825
18410	79.19	97.00	124.30	155.20	1.458	1.786	2.288	2.857
18415	79.76	97.70	125.20	156.32	1.469	1.799	2.306	2.870
18410	80.16	98.20	125.84	157.12	1.476	1.808	2.317	2.893
18405	80.57	98.70	126.48	157.92	1.483	1.816	2.328	2.906
18400	80.98	99.20	127.12	158.72	1.490	1.825	2.339	2.920
18395	81.18	99.45	127.44	159.12	1.494	1.830	2.344	2.927
18390	81.39	99.70	127.76	159.52	1.497	1.834	2.349	2.933
18385	81.50	99.95	128.08	159.92	1.500	1.838	2.355	2.940

The specific gravities were in each case estimated at exactly 15° C. and compared with water of 4°, the weighings being reduced to the vacuum. Special notice should be taken that all older tables (including those of Bineau, Otto, and Kolb) are entirely wrong in the case of the acids of highest strength, as the maximum of specific gravity does not (as it is made to do in those tables) coincide with the greatest strength, that is, pure monohydrated sulphuric acid, H_2SO_4 . The maximum is at about 98.5 per cent., and from this point the specific gravities decline to 100 per cent. H_2SO_4 ; above this point, that is when SO_3 is present, they instantly rise again. (Comp. Kohlrausch, Pogg. Annal. Ergänzungsband 8, p. 675; Schertel, Journ. f. prakt. Chemie [2], xxvi. p. 246; Lunge and Naef, Chem. Ind. 1883, p. 37, and others.)

Special attention should be drawn to the point that all tables indicate the specific gravities only for *chemically pure acids*; those of commercial impure acids are always higher; we shall come back to this point further on. The accuracy in the above-given table may be taken as ± 0.05 , so that the first decimal is right, but the second serves only for determining the first.

A paper by Mendelejeff (Zeitsch. f. physik. Ch. i. 273) on the specific gravities of mixtures of sulphuric acid and water has only theoretical interest.

A correction for any deviation of the temperature from 15° must be made, whenever the acid tested by the hydrometer is above or below that temperature. Bineau has given a small table for this purpose, which, however, is wrong for the more dilute acids. From a very large number of observations made in the Author's laboratory, a table has been constructed showing the alterations to be made in the specific gravities observed for all strengths of acid, and for all temperatures from 0° to 100°, in order to reduce them to 15° C. This table is found in Lunge and Hurter's 'Alkali-Maker's Pocketbook'; in this place we give only the average figures. For each degree above or below 15° you should add to or deduct from the specific gravity observed:—

0.0006	with acids up to 1.170
0.0007	with acids from 1.170 to 1.450
0.0008	„ „ 1.450 „ 1.580
0.0009	„ „ 1.580 „ 1.750
0.0010	„ „ 1.750 „ 1.840

All observers agree that the solutions of sulphuric acid contain different *hydrates*. The literature of this subject is very large, and we shall here quote only the most important facts (comp. also Mendelejeff, *supra*, p. 125, and Pickering, p. 118). A sesquihydrate of sulphuric acid cannot be established as a certain chemical compound, but the *double hydrate*, $\text{SO}_4\text{H}_2 + \text{H}_2\text{O}$, is known with certainty. It crystallizes from rather more dilute acid—for instance, acid of 144° Tw. in the cold. It contains 84.48 monohydrate + 15.52 water (or 68.97 anhydride + 31.03 water), melts at $+8^\circ$ C., but, owing to superfusion, generally only solidifies below this temperature (for instance, in the depth of winter); at 205° to 210° C. it already loses 1 mol. H_2O , and leaves ordinary oil of vitriol behind. The crystals form large clear hexagonal columns with six-pointed end-faces. Spec. grav. 1.78 to 1.79. By the crystallization of this hydrate carboys are often cracked in winter; acid of 144° Tw. and the like ought therefore only to be warehoused in places where the temperature will not sink too low, for instance below the acid-chambers. Stronger or weaker acid can be exposed to the cold of winter without any danger.

A third hydrate, $\text{SO}_4\text{H}_2 + 2 \text{H}_2\text{O}$, is assumed, because, on diluting strong vitriol with water down to this point (that is, corresponding to 73.13 per cent. monohydrate, or 59.70 per cent. of anhydride), the largest contraction, viz. from 100 volumes to 92.14 volumes, takes place. Bourgoin (Bull. Soc. Chem. [2] xii. 433) infers the same from observations on electrolyzing dilute vitriol. The density of this mixture is stated differently by different observers:—by Graham at 1.6321; by Bineau, 1.665; by Kolb, 1.652; by Jacquelin, 1.6746. According to Liebig it boils at 163° to 170° ; between 193° and 199° it loses one molecule of water, and is changed into $\text{SO}_3\text{H}_2 + \text{H}_2\text{O}$ (Graham).

Pickering (Chem. News, lx. p. 68) has obtained a hydrate of the formula $\text{H}_2\text{SO}_4, 4 \text{H}_2\text{O}$, containing 57.66 per cent. real sulphuric acid. It fuses at -25° . By adding a little water or sulphuric acid the fusing-point is at once lowered to -70° .

The specific gravities given in all the tables refer only to *pure* acid, and cannot be accepted as quite correct for the ordinary acid of trade, which always contains impurities. Kolb has examined into this matter, and has determined the influence of the common

impurities upon the density of sulphuric acid, viz. that of lead sulphate, of the oxygen compounds, of nitrogen, and of sulphurous acid. Arsenic, and perhaps iron, usually occur in too small a quantity in sulphuric acid to influence its density; but certainly there may be cases, not mentioned by Kolb, in which vitriol is *strongly* contaminated with salts of iron, aluminium, sodium, &c. The iron, for instance, may come from pyrites-dust; aluminium from the packing of the Glover tower, or from the fire-clay frequently employed for stopping leaks; sodium from solutions of nitrate or sulphate of soda, which sometimes get into the chambers by inadvertence.

For saturated solutions of *sulphurous acid* in sulphuric acid of varying density, Kolb gives the following table (Bull. Soc. Ind. de Mulhouse, 1872, p. 224)* :—

Density of Sulphuric Acid		Quantity of SO ₂ dissolved	
<i>before being saturated with SO₂.</i>	<i>after being saturated with SO₂.</i>	per kilog. Acid.	per litre Acid.
1·841	1·837	0·009 kilog.	5·8 litres.
1·839	1·881	0·014 "	8·9 "
1·540	1·541	0·021 "	11·2 "
1·407	1·419	0·032 "	15·9 "
1·227	1·244	0·068 "	29·7 "
1·000	1·041	0·135 "	49·9 "

In this table it strikes the attention that the saturation of *strong* acid with SO₂ somewhat lowers its specific gravity, but rather raises that of *weak* acid; with an acid of 1·540 both tendencies are at an equilibrium and the density is not changed.

J. T. Dunn (Chem. News, xliii. p. 121, and xlv. p. 270) has shown that Kolb's figures are too low. By passing a current of pure dry SO₂ through sulphuric acid of spec. grav. 1·841 he found that this acid dissolves :—

* The Table is corrected by dividing the last column by 10. The necessity of this correction is apparent on calculation, and especially on comparing the last figure (for pure water) with well-known facts.

Temperature.	Volume at 760 millim. pressure.	Spec. Grav. of solution at temp. of experiment.
At 11°·1 C.	33·78 vols. SO ₂	1·823
„ 16 ·1	28·86 „ „
„ 17 ·1	28·14 „ „
„ 26 ·9	19·27 „ „	1·822
„ 42 ·0	12·82 „ „	1·821
„ 50 ·9	9·47 „ „	1·818
„ 62 ·3	7·21 „ „	1·816
„ 84 ·2	4·54 „ „	1·809

Dilute acids dissolve the following quantities ; at temperatures varying from 15° to 16°, reduced to 760 millim. pressure :—

Spec. Grav. of sulphuric acid.	Absorbs vols. SO ₂ .
1·753	20·83
1·626	25·17
1·456	29·87
1·257	30·52
1·151	31·82
1·067	34·08

In such quantities (up to saturation) sulphurous acid certainly never occurs in commercial vitriol ; and it is very rarely that more than traces of it are found therein, since it does not agree with the *nitrogen oxides* which are most frequently found in commercial vitriol. *Nitric acid* is, if at all, only present in extremely small quantities in the vitriol of trade, and therefore does not modify its density to a sensible extent ; especially it will not be found in vitriol of more than 144°Tw., except *perhaps* in the nitrous vitriol from the Gay-Lussac towers ; but even this, according to my analyses (see below), under normal conditions contains mere traces of NO₃H. *Nitric oxide* can also be neglected ; neither concentrated nor diluted vitriol dissolves more than mere traces of it. *Nitrous acid* certainly has a very marked influence on the apparent percentage of a sulphuric acid, according to the hydrometrical test, although only in “nitrous vitriol” such large proportions of nitrous acid occur as to influence the specific gravity of the sulphuric acid. In order to estimate this influence, Kolb conducted into sulphuric acids of different concentrations a

mixture of dry air and dry nitric oxide in excess, supposing that it would only yield N_2O_3 , not NO_2 . His results were as follows * :—

Density of		100 parts of Acid contain				Quantity of SO_4H_2 which <i>pure</i> acid would contain if of equal spec. grav. as that saturated with N_2O_3 .
Pure Acid.	Acid saturated with N_2O_3 .	Before saturation.	After saturation.			
			N_2O_3 .	N_2O_3 .	SO_4H_2 .	
1·841	1·868	99·9	4·25	Traces.	94·5	?
1·793	1·814	86·2	4·12	1·28	82·8	89·2
1·749	1·751	81·4	3·90	1·55	76·2	81·4
1·621	1·628	70·7	2·30	1·10	68·6	71·0
1·512	1·519	60·7	0·74	0·31	60·2	61·5
1·426	1·434	52·7	0·25	0·24	53·0	53·6
1·327	1·336	42·2	0·11	0·76	40·8	43·4

R. Kisling (Chem. Ind. 1886, p. 137) has examined the effect of a percentage of *arsenic* on the specific gravity of sulphuric acid. The specific gravities of two commercial acids, A and B, were observed at $15^\circ C.$ and calculated for water of $4^\circ C.$ and the vacuum, in order to be comparable to Lunge and Naef's figures for pure acid (*suprà*, p. 119).

A.			B.		
Spec. grav. at 15° .	SO_4H_2 per cent.	As_2O_3 per cent.	Spec. grav. at 15° .	SO_4H_2 per cent.	As_2O_3 per cent.
1·8377	0·137	1·8387	93·82	0·024
1·8387	0·137	1·8372	93·67	0·035
1·8393	92·87	0·192	1·8373	93·12	0·028
1·8409	93·28	0·258	1·8384	93·72	0·037
1·8412	94·25	0·219	1·8386	93·96	0·037
1·8413	93·60	0·254	1·8388	94·04	0·039
1·8414	93·93	0·231
1·8415	93·77	0·231

* Unfortunately this table is of little practical use, even making the (very hazarded) assumption that the respective quantities of N_2O_3 and N_2O_5 , for which at that time no very trustworthy methods were in existence, are correctly stated; for by the above method undoubtedly varying quantities of N_2O_3 and N_2O_5 would be formed, and would dissolve in the sulphuric acid, whilst the "nitrous vitriol," under ordinary circumstances, contains little or no nitric acid, as we shall see later on.

When comparing these results with those of Lunge and Naef, the considerable influence of the arsenious acid on the specific gravity of sulphuric acid is very apparent.

With respect to *lead sulphate* Kolb found that, at the ordinary temperature, there were dissolved in

100	parts	vitriol	of	1.841	spec. grav.	0.039	part.
100	"	"	"	1.793	"	0.011	"
100	"	"	"	1.540	"	0.003	"

In more dilute acids the lead can hardly be estimated. Nitric acid, which anyhow occurs in very small quantities, does not strongly influence the solubility of lead sulphate in sulphuric acid, nitrous acid not at all. The influence of lead sulphate on the density of vitriol can accordingly be neglected for the ordinary temperature; at most it would influence the fourth place of decimals.

Although, as we see, the impurities of ordinary sulphuric acid, leaving aside "nitrous vitriol," have very little influence on its density, still the latter, at the highest degrees of concentration, is no trustworthy means of estimating the percentage of real SO_4H_2 in the acid, even when the correction for temperature mentioned on page 125 is applied, because at this concentration a small difference in density corresponds to a very large difference in percentage. Many factories have special hydrometers, in which the last few degrees are spread over a large area and are subdivided further; but in fact the density ought to be estimated by more accurate methods, for the hydrometers are frequently not reliable, and certainly not so unless the normal temperature for which they have been made be *exactly* observed. But any determination of density for estimating the percentage of the very strongest acids must be rejected, after what we have seen on p. 125. The acids from 96 per cent. upwards ought therefore always to be estimated alkalimetrically.

The following table of Anthon's will be of practical value. It shows in column *a* how many parts of oil of vitriol of 168°Tw . must be mixed with 100 parts water at 15° or 20° in order to obtain an acid of the specific gravity *b*.

a.	b.	a.	b.	a.	b.
1	1·009	130	1·456	370	1·723
2	1·015	140	1·473	380	1·727
5	1·035	150	1·490	390	1·730
10	1·060	160	1·510	400	1·733
15	1·090	170	1·530	410	1·737
20	1·113	180	1·543	420	1·740
25	1·140	190	1·556	430	1·743
30	1·165	200	1·568	440	1·746
35	1·187	210	1·580	450	1·750
40	1·210	220	1·593	460	1·754
45	1·229	230	1·606	470	1·757
50	1·248	240	1·620	480	1·760
55	1·265	250	1·630	490	1·763
60	1·280	260	1·640	500	1·766
65	1·297	270	1·648	510	1·768
70	1·312	280	1·654	520	1·770
75	1·326	290	1·667	530	1·772
80	1·340	300	1·678	540	1·774
85	1·357	310	1·689	550	1·776
90	1·372	320	1·700	560	1·777
95	1·386	330	1·705	580	1·778
100	1·398	340	1·710	590	1·780
110	1·420	350	1·714	600	1·782
120	1·438	360	1·719		

On mixing oil of vitriol with water a considerable rise of temperature takes place, water being chemically fixed by the formation of certain hydrates, as described above. Besides, on mixing concentrated acid with water, as already mentioned, a not inconsiderable contraction takes place, which must equally lead to an evolution of heat. But on mixing strong vitriol with snow a strong cold is produced by the heat becoming latent on the liquefaction of snow, which considerably exceeds that becoming free in consequence of the chemical combination. This cold, however, is only produced when the proportion between acid and ice does not exceed certain limits: for 1 part of vitriol there must be $1\frac{1}{4}$ part of snow present; with less snow there is a rise of temperature.

Even at stronger dilution much heat is liberated. Many observers have worked upon this subject; but we quote here only the results of Thomsen (Deutsch. chem. Ges. Ber. iii. p. 496), who states that one gramme-molecule (that is, 98 grammes) H_2SO_4 gives the following amounts of heat when combining with x molecules of water:—

<i>x.</i>			
1	6272	metrical heat-units.
2	9364	„ „
3	11108	„ „
5	13082	„ „
9	14940	„ „
19	16248	„ „
49	16676	„ „
99	16850	„ „
199	17056	„ „
499	17304	„ „
799	17632	„ „
1599	17848	„ „

Somewhat higher results have been obtained by Pickering (J. Chem. Soc. lvii. p. 94).

On account of this considerable evolution of heat, concentrated vitriol and water must always be mixed with care: the water ought never to be poured into the acid, but the acid run in a thin jet into the water with constant stirring. On a sudden mixture, so much heat is liberated at once that the acid may be raised to the boiling-point and splash about; and glass vessels are easily cracked thereby.

The affinity of vitriol for water is also proved by its great hygroscopicity. Concentrated vitriol is one of the best means for drying gases; and it is not only used in this way for innumerable scientific, but also for some technical purposes—for instance, in the manufacture of chlorine by Deacon's process, where the gaseous mixture, having been deprived of its hydrochloric acid by water, is passed through a coke-tower fed with sulphuric acid, in order to be deprived of its moisture. In the same way, chlorine gas is dried for the process of utilizing tinned scrap-iron by treatment with chlorine, which in the dry state does not act upon iron, but gives with tin anhydrous tin tetrachloride.

Concentrated sulphuric acid acts also upon liquid and solid bodies by depriving them of water or even splitting off the elements of the same if the substance only contains the latter, but no readily formed water. Upon this action, too, a host of scientific and technical applications of sulphuric acid are founded. In this case frequently the so-called *sulphonic acids* are formed, generally com-

pounds easily lending themselves to further reactions. Instances of this are:—the formation of ether by the splitting-up of sulphuric acid, with the intermediate formation of sulphovinic acid; that of ethylene on the further splitting-off of water; the preparation of nitrobenzene, picric acid, nitronaphthalene; the manufacture of resorcine and alizarine by the alkaline fusion of the sulphonic acids of benzene and anthraquinone, and many other cases.

The charring of many organic substances, such as wood, sugar, &c., by contact with strong vitriol, is derived from the same source. Necessarily this acid, in its concentrated form, must have an extremely prejudicial action on the animal body. The remedy usually applied, viz. burnt magnesia, cannot do much good when the epithelium of the œsophagus and the stomach are once destroyed.

The affinity of concentrated vitriol for water is also shown by the fact that it easily runs over, when kept in open vessels, by attracting moisture from the air—a fact to keep in view in the case of balances &c.

The *melting-points* of sulphuric acids of different degrees of concentration are given by Payen as follows (but not all of his statements agree with the results of more recent researches as quoted above):—

Anhydride, α modification	melts at	+ 18	°C.
„ β „	„	+ 100	
Subhydrate (pyrosulphuric acid)	„	+ 35	
Monohydrate, SO_4H_2	„	+ 10·5	
The same with a very small addition of anhydride	}	— 20	
„			
The same, with a very little water (ordinary oil of vitriol)	}	— 20 to — 30	
„			
Dihydrate	„	+ 8·5	
Sulphuric acid containing, to 1 molecule of acid, 3 molecules of water or more, remains solid at	}	— 20	
„			
The same, <i>in vacuo</i>	„	— 40	

I have made a new determination of the freezing- and melting-

points of various strengths of sulphuric acid (Berl. Ber. 1881, p. 2649), with the following results:—

Spec. grav. of acid at 15° C.	Freezing-point.	Melting-point.
1·671 . . .	liquid at -20° C.	liquid.
1·691 . . .	do.	do.
1·712 . . .	do.	do.
1·727 . . .	-7·5°	-7·5°
1·732 . . .	-8·5	-8·5
1·749 . . .	-0·2	+4·5
1·767 . . .	+1·6	+6·5
1·790 . . .	+4·5	+8·0
1·807 . . .	-9·0	-6·8
1·822 . . .	liquid at -20° C.	liquid.
1·840 . . .	do.	do.

Pickering (J. Chem. Soc. 1890, lvii. p. 331 *et seq.*) has published an extensive memoir on the freezing-points of sulphuric acid and its solutions. We here give a few of the results obtained (from his table, p. 365), but we must remark that the apparently extreme accuracy of the estimations is quite illusory, since, even with the best methods known and the greatest skill, a *reliable* estimation of the strength of sulphuric acid can only be made up to the *first* decimal of the percentage amount, the second decimal being uncertain by ± 5 , whilst in that memoir *four* decimals are given! The third decimal of the thermometric estimation must be equally uncertain.

Percent. H_2SO_4 .	Mols. H_2O to 100 H_2SO_4 .	Freezing-point.	Percent. H_2SO_4 .	Mols. H_2O to 100 H_2SO_4 .	Freezing-point.
100	0	10·352	94·922	29·10	-24·75
99·6007	2·18	8·053	94·084	34·56	-33·0
99·0440	5·26	4·649	93·556	37·52	-38·0
98·5346	8·10	1·591	90·566	56·74	-10·202
98·0316	10·91	-1·676	88·0355	74·01	+2·768
97·4318	14·36	-5·349	84·9717	96·33	+8·468
97·0257	16·70	-8·087	84·6055	99·11	+8·513
96·1171	21·80	-13·686	80·6767	130·45	+2·217
95·5205	25·54	-18·275	75·8940	173·00	-15·199

On *boiling* dilute sulphuric acid, at first nothing but aqueous

vapour escapes; according to Graham, only then is acid vapour mixed with the steam, when no more than 2 molecules of water are present to 1 of SO_3 —that is, with a percentage of 84.48 SO_4H_2 or a specific gravity of 1.78. After several discussions about the loss of sulphuric acid in concentrating it, by myself, Bode, Walter, &c., it may be assumed that in manufacturing practice no sensible loss of acid takes place by real *volatilization* up to a strength of 144° or even of 152° Tw.; but from violently boiling acid there is always a little acid carried away mechanically in the shape of small drops, especially in pans fired from the top and also in the Glover tower. When the evaporation up to that point takes place quietly at a moderate heat, there is probably no loss of acid at all.

The *boiling-point* of sulphuric monohydrate is stated by Marignac = 338°, by Pfaundler = 317°. The boiling-points of sulphuric acid containing water were examined by Dalton in the beginning of this century. His table, which was obviously wrong, has been replaced by another, founded upon the author's investigations (Berl. Ber. xi. p. 370).

TABLE I.

Specific gravity.	Temperature. °C.	Spec. grav. reduced to 15° C.	Percentage of SO_4H_2 .	Boiling-point. °C.	Barometer reduced to 0°; millims.
1.8380	17	1.8400	95.3	297	718.8
1.8325	18.5	1.8334	92.8	280	723.9
1.8240	15.5	1.8245	90.4	264	720.6
1.8130	16	1.8140	88.7	257	726.0
1.7985	15.5	1.7990	86.6	241.5	720.1
1.7800	15	1.7800	84.3	228	720.5
1.7545	16	1.7554	81.8	218	726.0
1.7400	15	1.7400	80.6	209	720.6
1.7185	17	1.7203	78.9	203.5	725.9
1.7010	18	1.7037	77.5	197	725.2
1.6750	19	1.6786	75.3	183.5	725.2
1.6590	16	1.6599	73.9	180	725.2
1.6310	17	1.6328	71.5	173	725.2
1.6055	17	1.6072	69.5	169	730.1
1.5825	15	1.5825	67.2	160	728.8
1.5600	17	1.5617	65.4	158.5	730.1
1.5420	17	1.5437	64.3	151.5	730.1
1.4935	18	1.4960	59.4	143	730.1
1.4620	17	1.4635	56.4	133	730.1
1.4000	17	1.4015	50.3	124	730.1
1.3540	17	1.3554	45.3	118.5	730.1
1.3180	17	1.3194	41.5	115	730.1
1.2620	17	1.2633	34.7	110	732.9
1.2030	17	1.2042	27.6	107	732.9
1.1120	17	1.1128	15.8	103.5	732.9
1.0575	17	1.0580	8.5	101.5	735.0

TABLE II.

(Calculated by graphical interpolation.)

Percent. SO ₄ H ₂ .	Boiling- point.	Percent. SO ₄ H ₂ .	Boiling- point.	Percent. SO ₄ H ₂ .	Boiling- point.	Percent. SO ₄ H ₂ .	Boiling- point.
5	101	45	118.5	70	170	86	238.5
10	102	50	124	72	174.5	88	251.5
15	103.5	53	128.5	74	180.5	90	262.5
20	105	56	133	76	189	61	268
25	106.5	60	141.5	78	199	92	274.5
30	108	62.5	147	80	207	93	281.5
35	110	65	153.5	82	218.5	94	288.5
40	114	67.5	161	84	227	95	295

The *tension of aqueous vapour* in sulphuric-acid solutions of various strengths was determined by Regnault in 1845 (*Ann. de Chim.* [3], xv. p. 179) for temperatures from 5 to 35° C. We here give his table (for every other degree), adding to the hydrates quoted by him the percentage composition and specific gravities. We also subjoin Sorel's table, computed for a wider interval of temperatures, better suited for the wants of sulphuric-acid manufacture. The tensions are stated in millimetres of mercurial pressure.

Regnault's Table of the Aqueous-Vapour Tensions of Dilute Sulphuric Acid.

°C.	H ₂ SO ₄ +H ₂ O 84.5°/o 1.780.	H ₂ SO ₄ +2H ₂ O 73.1°/o 1.654.	H ₂ SO ₄ +3H ₂ O 64.5°/o 1.554.	H ₂ SO ₄ +4H ₂ O 57.6°/o 1.477.	H ₂ SO ₄ +5H ₂ O 52.1°/o 1.420.	H ₂ SO ₄ +7H ₂ O 43.7°/o 1.340.	H ₂ SO ₄ +9H ₂ O 37.7°/o 1.287.	H ₂ SO ₄ +11H ₂ O 33.1°/o 1.247.	H ₂ SO ₄ +17H ₂ O 24.3°/o 1.176.
5	0.105	0.388	0.861	1.294	2.137	3.168	4.120	4.428	5.478
7	0.108	0.430	0.985	1.510	2.464	3.643	4.728	5.164	6.300
9	0.112	0.476	1.125	1.753	2.829	4.176	5.408	5.980	7.216
11	0.118	0.527	1.280	2.025	3.240	4.773	6.166	6.883	8.237
13	0.124	0.586	1.454	2.331	3.699	5.443	7.013	7.885	9.374
15	0.131	0.651	1.648	2.674	4.215	6.194	7.958	8.995	10.641
17	0.139	0.725	1.865	3.059	4.793	7.036	9.014	10.222	12.054
19	0.149	0.808	2.108	3.492	5.440	7.980	10.191	11.583	13.628
21	0.159	0.901	2.380	3.977	6.166	9.039	11.506	13.090	15.383
23	0.171	1.006	2.684	4.523	6.979	10.228	12.974	14.760	17.338
25	0.184	1.125	3.024	5.135	7.892	11.557	14.613	16.610	19.516
27	0.199	1.258	3.405	5.822	8.914	13.050	16.443	18.659	21.944
29	0.216	1.408	3.830	6.594	10.060	14.723	18.485	20.929	24.650
31	0.235	1.557	4.305	7.459	11.345	16.600	20.765	23.443	27.666
33	0.256	1.767	4.838	8.432	12.785	18.704	23.311	26.228	31.025
35	0.280	1.981	5.432	9.524	14.400	21.063	26.152	29.314	3.770

Spec. Grav. of Acid.	Approx. degree of Twad- dall.	Per- cent. of H ₂ SO ₄ .	Temperatures (° C.).																	
			10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°	85°	90°	95°
1.342	68½	44	mm. 4.4	mm. 6.1	mm. 8.5	mm. 11.5	mm. 15.5	mm. 20.9	mm. 28.1	mm. 37.4	mm. 48.3	mm. 59.6	mm. 76.5	mm. 96.4	mm. 107.2	mm. 132.1	mm. 152.0	mm. 192.6	mm. 236.7	mm. 251.5
1.361	72	46	4.0	5.5	7.7	10.5	14.5	19.7	26.3	33.6	44.4	59.6	76.5	96.4	107.2	132.1	152.0	192.6	236.7	251.5
1.380	76	48	3.7	5.0	7.1	9.6	13.4	18.1	23.9	30.5	40.1	53.5	69.0	86.8	96.4	118.1	152.0	192.6	236.7	251.5
1.399	80	50	3.3	4.5	6.5	8.8	12.0	16.4	21.4	27.4	35.9	47.4	61.3	77.0	84.5	104.5	131.2	166.5	207.9	222.0
1.418	83½	52	3.0	4.0	5.8	7.9	10.9	14.5	18.9	24.1	31.5	41.5	54.0	67.9	74.8	92.6	116.1	146.8	183.5	222.0
1.439	88	54	2.6	3.6	5.0	7.0	9.5	12.5	16.5	21.3	27.8	36.2	47.2	59.9	65.0	80.6	100.9	128.2	160.0	195.0
1.459	92	56	2.2	3.1	4.3	6.0	8.1	11.0	14.2	18.5	24.1	31.0	41.6	51.6	55.4	68.4	86.2	110.6	138.5	169.5
1.480	96	58	1.9	2.6	3.5	5.1	7.2	9.1	12.0	15.8	20.4	26.1	34.5	44.0	46.1	56.7	72.3	94.0	118.7	146.0
1.502	100½	60	1.6	2.1	3.0	4.3	6.1	7.5	10.0	13.0	16.9	21.6	28.7	36.7	37.7	46.2	59.7	78.2	100.7	125.0
1.525	105	62	1.4	1.8	2.6	3.6	5.0	6.5	8.1	10.5	13.9	17.7	23.9	30.0	30.3	37.4	48.0	63.8	83.7	105.0
1.547	109½	64	1.2	1.6	2.2	3.0	4.0	5.5	6.5	8.2	10.9	14.0	18.7	23.9	24.2	30.3	39.0	52.5	70.0	88.0
1.569	114	66	1.1	1.4	1.8	2.5	3.5	4.5	5.4	6.5	8.9	11.5	15.2	19.1	19.4	24.4	31.4	42.5	56.0	72.0
1.592	118½	68	0.9	1.2	1.5	2.1	3.0	3.8	4.5	5.4	7.2	9.5	12.3	15.4	15.5	19.8	25.5	33.9	44.4	57.0
1.615	123	70	0.8	1.0	1.3	1.8	2.5	3.3	3.8	4.4	5.9	7.5	9.5	12.1	12.0	15.4	20.0	26.2	33.7	43.4
1.638	127½	72	0.7	0.8	1.0	1.4	2.0	2.8	3.2	3.6	4.8	6.0	7.5	9.5	9.5	12.1	15.4	19.5	24.5	31.5
1.662	132½	74	0.5	0.6	0.6	1.2	1.7	2.1	2.6	3.1	3.9	4.9	6.0	7.5	7.5	9.5	11.8	15.0	18.5	22.0
1.687	137½	76	0.4	0.4	0.5	1.0	1.4	1.8	2.1	2.5	3.0	4.0	4.8	5.9	5.7	7.0	8.5	10.5	13.0	15.8
1.710	142	78	0.3	0.3	0.4	0.8	1.1	1.4	1.7	2.1	2.4	3.0	3.5	4.0	4.1	5.0	6.2	7.5	9.3	11.0
1.733	146½	80	0.2	0.2	0.3	0.6	0.8	1.1	1.3	1.6	1.9	2.4	2.9	3.3	3.3	4.1	5.0	6.2	7.5	9.3
1.755	151	82	0.1	0.1	0.2	0.4	0.5	0.5	0.9	1.1	1.4	1.7	2.0	2.3	2.7	3.2	3.9	4.7	5.6	6.8

The *specific heat* of monohydrated sulphuric acid at 16°–20° C. is 0·3315 (water=1). Marignac states the specific heat of acid diluted with water as follows:—

$\text{H}_2\text{SO}_4 +$	5 aq.	=0·5764
„	10 „	0·7212
„	15 „	0·7919
„	25 „	0·8537
„	50 „	0·9155
„	100 „	0·9545
„	200 „	0·9747
„	400 „	0·9878

The following table, by Bode, is more convenient for practical use (*Zeitschr. f. angew. Chem.* 1889, p. 244):—

Spec. grav.	Spec. heat.	Spec. grav.	Spec. heat.
1·842	0·3315	1·020	0·67
1·774	0·38	1·263	0·73
1·711	0·41	1·210	0·78
1·615	0·45	1·162	0·82
1·530	0·49	1·116	0·87
1·442	0·55	1·075	0·90
1·383	0·60	1·037	0·95

Comp. also Pickering (*J. Chem. Soc.* lvii. p. 90).

Decompositions of Sulphuric Acid.—Some of these have been mentioned already—for instance, that into anhydride and water by evaporation. The mixed vapour, on account of the unequal velocity of diffusion of the two vapours, can be separated to a great extent into its two constituents, so that at 520° C., in an hour, a residue of 60 per cent. monohydrate and 40 per cent. anhydride, at 445° C. 75 per cent. monohydrate and 25 per cent. anhydride was obtained (Wanklyn and Robinson, *Proc. Roy. Soc.* xii. p. 507). Perhaps a process for preparing fuming acid can be founded upon this fact. Even far below the boiling-point the dissociation begins in the liquid acid. It has been pointed out that already at 30° to 40° C. the hydrate begins to give off vapours of anhydride (Marignac), which fact has been confirmed by the exact researches of Dittmar (*Chem. Soc. Journ.* [2] vii. p. 446) and Pfaundler and Pölt (*Zeitschr. f. Chemie*, xiii. p. 66).

A more thorough decomposition into sulphur dioxide, oxygen, and water takes place on conducting the vapour of sulphuric acid through porcelain or platinum tubes, filled with bits of porcelain and heated to a bright red heat. This mode of decomposition has been recommended by Deville and Debray as a "cheap" plan for making oxygen; but it does not seem to have answered, owing to the insufficient sale of sulphurous acid or its salts; it was expected to play a great part in the manufacture of anhydride by Winkler's process, but even for this purpose it has not been found economical.

On heating with charcoal to 100° or up to 150° C., sulphuric acid yields carbon dioxide and sulphur dioxide; on boiling with phosphorous, sulphur; on boiling with sulphur, sulphur dioxide; by the action of the electric current, hydrogen, oxygen, sulphur, &c. (in dilute sulphuric acid the electric current merely causes the decomposition of water).

Sulphuric acid at temperatures below its boiling-point behaves as the strongest of all acids, and expels all other acids from their salts when the solubilities &c. allow this; but, inversely, sodium sulphate is also decomposed by hydrochloric acid. In fact, the "avidity" of hydrochloric and nitric acid at ordinary temperatures much exceeds that of sulphuric acid. Boussingault (Ann. Chim. Phys. [5] ii. p. 120) has shown that dry hydrochloric-acid gas at a red heat decomposes the sulphates of sodium, potassium, barium, strontium, and calcium (see further on). More refractory acids expel sulphuric acid at higher temperatures—for instance, boric acid, silica, and phosphoric acid.

With the bases sulphuric acid forms two principal series of salts, viz. acid ones, of the formula $\text{SO}_2 \begin{smallmatrix} \text{OH} \\ \diagdown \\ \text{OM} \end{smallmatrix}$, and neutral ones, of the formula $\text{SO}_2 \begin{smallmatrix} \text{OM} \\ \diagdown \\ \text{OM} \end{smallmatrix}$. Very frequently it also occurs in basic salts, rarely in hyperacid salts.

The technical applications of sulphuric acid to a great extent rest on its great affinity to all bases. Of its salts the acid and neutral ones are soluble in water, excepting the neutral salts of barium, strontium, lead, silver, and mercury (in the state of protoxide), which are little or not at all soluble in water and dilute acids. Calcium sulphate is sparingly soluble in water. Most sulphates are insoluble in alcohol. The *basic* sulphates are mostly insoluble in water, but soluble in acids. The sulphates incline very much towards the formation of double salts, of which those

are called *alums* which contain a combination of univalent and trivalent (corresponding to a double atom of quadrivalent) metals.

The neutral salts of the alkali-metals, of calcium, magnesium, silver, manganese, and ferrous, the latter only if entirely free from acid and peroxide (a condition very rarely realized), do not redden blue litmus-paper, whilst all other soluble sulphates do this.

On *heating* to a red heat, only the neutral sulphates of the alkalis, of the alkaline earths, and of lead remain unchanged. At a still higher temperature (that of melting iron) the two latter classes are also decomposed, but the alkaline sulphates are volatilized without a change. Even zinc and manganous sulphate are difficult to decompose. This explains the difficulty of completely converting blende into oxide of zinc.

On roasting, the decomposable sulphates yield metallic oxides, sulphur dioxide, and oxygen. They are much more easily split up on heating by certain additions, such as coal, iron, &c.

On the metals sulphuric acid acts in a very different way. The water-decomposing metals in the cold yield nothing but hydrogen with it; in the hot even zinc and iron already yield sulphurous acid; and zinc, if certain conditions are observed, can even yield sulphuretted hydrogen (Fordos and Gélis).

Most of the heavy metals do not act upon sulphuric acid in the cold and [in a dilute state; they yield sulphur dioxide only on being heated with *concentrated* acid, such as arsenic, antimony, bismuth, tin, lead, copper, mercury, silver (sulphates being formed at the same time); gold, platinum, iridium, and rhodium do not act on sulphuric acid at any temperature.

While *pure* sulphuric acid has practically no action whatever on *platinum*, even at its boiling-point, there is some action exercised by the impurities never absent from commercial acid. We shall go into this matter when treating of the concentration of sulphuric acid in platinum vessels.

The behaviour of *cast-iron* towards sulphuric acid is of great technical importance. It has been known for many years past that concentrated oil of vitriol acts very little indeed upon cast-iron, whether hot or cold, provided that the access of air is excluded, whose moisture would dilute the acid and cause it to act more strongly. It was, however, at first considered an extremely bold step when Lancashire alkali-makers began to decompose

common salt with sulphuric acid in cast-iron pots, as is explained in the Chapter treating of the manufacture of salt-cake.

Since that period manufacturers have become much bolder, and for many years past cast-iron vessels have been employed for "parting" alloys of silver and gold by boiling sulphuric acid, for making nitrobenzene and analogous products by a mixture of strong sulphuric and nitric acid, and innumerable other purposes where strong acids have to be manipulated either hot or cold, even for the last concentration of sulphuric acid itself. Dilute sulphuric acid, if the dilution be not too strong, acts very little on cast-iron in the cold or at a gentle heat, if air be excluded; it can hence be employed for "acid-eggs," in which chamber-acid is forced up, in lieu of pumps, and similar purposes.

It is usually assumed that some descriptions of cast-iron resist the attack of acids more than others. This point, together with some others of importance, has been the subject of experiments made in my laboratory (Chem. Industrie, 1886, p. 47), of which the following is an abstract.

Samples of various mixtures, employed for ordinary castings, were procured from iron-founders, and were shaped into small cylinders of exactly the same size, so as to offer always the same surface to the attack of the acid. The access of air was excluded in all cases, and the duration of the experiment was just an hour in each case. The mixtures employed were:—

- No. 1. White and grey charcoal-pig, melted in the cupola.
- No. 2. The same, cast very cold.
- No. 3. Ordinary machine-casting, containing one third of scrap-iron.
- No. 4. Hard (chilled) casting (special mixture).
- No. 5. 150 Clarence No. 3, 200 Hayenge No. 3, 200 scrap.
- No. 6. 200 Clarence No. 3, 75 Hayenge No. 3, 225 scrap.
- No. 7. 200 Harrington No. 4, 200 Coltness No. 1, 100 scrap.
- No. 8. Coltness No. 1 pure.

("Clarence" comes from the North of England, near Middlesbrough; "Harrington" is Cumberland hematite pig; "Coltness" is Scotch pig; "Hayenge" is Lorraine pig.) The following table shows the percentage loss of weight caused by an hour's action of sulphuric acid of various strengths and qualities at different temperatures:—

Mixture No.	a.			b.			c.		
	Pure acid 168° Tw.			Pure acid 142° Tw.			Pure acid 106° Tw.		
	20° C.	100° C.	295° C.	20° C.	100° C.	200° C.	20° C.	100° C.	147° C.
1	0.016	0.096	0.075	0.018	0.156	1.539	0.015	0.285	1.107
2	0.028	0.099	0.103	0.016	0.160	1.581	0.026	0.277	1.083
3	0.021	0.084	0.046	0.016	0.125	2.551	0.025	0.324	2.053
4	0.017	0.082	0.096	0.010	0.154	1.551	0.027	0.236	1.323
5	0.023	0.117	0.131	0.016	0.158	2.229	0.027	0.320	1.667
6	0.020	0.103	0.131	0.019	0.146	2.082	0.022	0.314	1.615
7	0.021	0.080	0.175	0.025	0.148	2.595	0.027	0.343	1.715
8	0.025	0.100	0.133	0.017	0.149	2.639	0.037	0.323	1.952
Average	0.021	0.095	0.113	0.018	0.149	2.096	0.026	0.300	1.564

Mixture No.	<i>d.</i>		<i>e.</i>	<i>f.</i>	<i>g.</i>
	Commercial acid.				Acid of 168° Tw. containing some sodium sulphite.
	168° Tw. 100° C.		142° Tw. 200° C.	106° Tw. 174° C.	295° C.
2	0.094	0.139	2.017	1.114	0.107
4	0.089	0.124	2.007	1.368	0.107
5	0.102	0.156	2.248	1.671	1.106
6	0.074	0.152	2.645	1.981	0.136
Average	0.085	0.143	2.229	1.533	0.109

These experiments lead to the following conclusions :--

(1) At the ordinary temperature all acids down to 106° Tw. act very little on all descriptions of cast-iron.

(2) At 100° C. the action is much stronger. It is least in the case of acid of 168° Tw., $1\frac{1}{2}$ times stronger with acid 142° Tw., and 3 times stronger with acid 106° Tw.

(3) At the boiling-point the differences are far more pronounced. Acid of 168° Tw. acts very little even then, both in the pure state, or as commercial acid (containing a little N_2O_3), or when containing a little SO_2 . But acid of 142° Tw. acts $\frac{1}{4}$ times stronger at 200° than the same acid at 100° C., and 20 times stronger than acid of 168° Tw. At 285° C. commercial acid of

142° Tw. does not act very differently from pure acid of the same strength. Acid of 106° Tw. at its boiling-point (=147° C.) acts less than acid of 142° Tw. at 200° C., but still 14 times as much as acid of 168° Tw. at 295° C. There is no difference between pure and commercial acid in this case.

(4) The differences between various mixtures of cast-iron are of no importance against acid of 168° Tw. in all cases, and against the weaker acids at 20° and 100° C. But the latter acids at their boiling-point act decidedly less on charcoal-pig and on chilled cast-iron than on all other kinds. A difference between hot and cold casting could not be found. The strongest attack was made on Scotch pig and on mixtures containing such.

In another series of tests we examined the action of *mono-hydrated sulphuric acid* on various metals, both on standing 6 days at 20° and on heating 2 hours to 100° C., always with exclusion of air. The loss of weight was :—

	Loss per cent.		Loss in grams per square centimetre of surface.	
	6 days at 20° C.	2 hours at 100° C.	6 days at 20° C.	2 hours at 100° C.
Cast-iron.....	0·041	0·071	0·062	0·015
Wrought-iron...	0·175	0·313	0·056	0·095
Copper	2·630	excessive	1·115	excessive
Lead	3·480	3·650	1·790	1·847

Wrought-iron is much more acted upon than cast-iron, but at the ordinary temperature it completely resists the action of strong sulphuric acid down to 140° Tw., and probably even a little below that strength. Where, however, through the action of moist atmospheric air, the acid gets more diluted, a very strong action sets in. Hence the wrought-iron vessels in which sulphuric acid is now very generally carried must be protected inside against any access of air when empty, and at the man-holes &c., where temporary access of air is unavoidable, they are best protected by a sheet of lead.

The action of sulphuric acid on lead has been the subject of many experiments. Calvert and Johnson (Compt. Rend. lvi. p. 140) found the following results of ten days' action of pure acid (Nos. I. to IV.) at ordinary temperatures, and of commercial acid

(Nos. V. and VI.) at a temperature of 48° to 50° , on a superficial metre of lead, expressed in grams of the PbSO_4 formed :—

	Spec. grav. of the acid employed.	Ordinary lead. grms.	Virgin lead. grms.	Pure lead. grms.
I.	1.842	67.70	184.20	201.70
II.	1.705	8.35	16.50	19.70
III.	1.600	5.55	10.34	16.20
IV.	1.526	2.27	4.34	6.84
V.	1.746	49.67	50.84	55.00
VI.	1.746	51.91	54.75	57.41

The result is that lead is all the more acted upon the purer it is, and that an energetic action only takes place above the specific gravity of 140° Tw.

Similar results were obtained by Mallard (Bull. Soc. Chem. 1874, ii. p. 114) and Hasenclever.

Bauer (Berl. Ber. 1875, p. 210) found that 50 grams of strongest oil of vitriol (168° Tw.) with 0.2 gram of pure lead produced a sensible evolution of gas at 175° , stronger at 196° ; at 230° – 240° suddenly all the lead is changed into sulphate, with formation of SO_2 , H and S.

Lead containing varying quantities of bismuth (0.71 or 4 or 10 per cent.) was even more strongly acted upon, whilst small quantities of antimony and copper make the lead more resisting; platinum acts in a similar way. Lead containing 10 per cent. tin behaves like pure lead.

According to experiments made by J. Glover (Chem. News, xlv. p. 105), pure lead is less acted upon when suspended in a vitriol chamber than such containing 0.1 to 0.75 per cent. copper, or 0.1 to 0.5 per cent. antimony. N. Cookson (ibid. p. 106) found that strong acids at a high temperature act more upon lead containing antimony than upon pure lead, whilst weaker acid at a lower temperature acts the other way. Since Glover's and Cookson's experiments are in direct contradiction with the results obtained by many previous observers, this matter ought to be cleared up by further tests*. Comp. also Mactear (Chem. News, xli. p. 236).

* Experiments made in my laboratory on this subject will be given in the Appendix.

In the north of England those rolling-mills which roll the sheet-lead for the vitriol-works supply a special kind of "chemical lead" which is made from the melted-up old chamber-lead, pipes, &c.; in this case many impurities, especially antimony, from "regulus"-valves, &c., get into the lead, which are supposed to improve its quality for acid-chambers.

Napier and Tatlock (Chem. News, xlii. p. 314) found that the action of sulphuric acid on lead at the ordinary temperature is accompanied by an evolution of hydrogen which may cause bulging out of the closed lead vessels in which the acid is sometimes sent out for sale.

Muir and Robbs (Chem. News, xlv. p. 70) found that *zinc* in contact with acid of the formula SO_4H_2 , 5 H_2O yields hydrogen containing still a little H_2S ; with SO_4H_2 , 6 H_2O pure hydrogen. *Tin* is not acted upon by acid of the formula SO_4H_2 , 3 H_2O .

Selenium is pretty frequently found in commercial sulphuric acid. Such acid may cause trouble in some cases, for instance in purifying mineral oils (comp. Drinkwater, Analyst, viii. p. 63; the quantity of 0.5 per cent. selenium there stated seems almost incredibly high).

Behaviour of Sulphurous and Sulphuric Acid towards the Oxides of Nitrogen.—The reactions between the oxides and acids of sulphur and nitrogen are of extreme importance for the theory of the sulphuric acid process in general, and for the recovery of the nitrogen compounds in particular.

The older researches in this field, of Clément-Desormes, Dalton, Davy, Berzelius, Gay-Lussac, W. Henry, Gaultier de Claubry, De la Provostaye, A. Rose, Koene, Weltzien, Rebling, and Müller, have now merely an historical interest. The modern literature of this subject begins with the labours of R. Weber, during the years 1862 to 1867, published in the Journ. f. prakt. Chem. lxxxv. p. 423 and c. p. 37; Poggendorff's Annalen, cxxiii. p. 341, cxxvii. p. 543, cxxx. p. 277, and partly in Dingler's Polyt. Journal, clxvii. p. 453. Other very important papers have been published by Cl. A. Winkler ('Researches on the Chemical Processes going on in the Gay-Lussac Towers,' Freiberg, 1867), by Rammelsberg (Ber. d. deutsch. chem. Gesellsch. 1872, p. 310), by Michaelis and Schumann (ib. 1874, p. 1075).

My own researches referring to this subject are found in the following publications:—1877: Berl. Ber. x. p. 1073 and 1432.

1878: Berl. Ber. xi. pp. 434 & 1229; Dingler's Journal, ccxxviii. pp. 70, 548, & 553. 1879: Dingler's Journal, ccxxxiii. p. 63; Berl. Ber. xii. pp. 357 & 1058. 1881: Berl. Ber. xiv. pp. 2188 & 2196. 1882: Berl. Ber. xv. pp. 488 & 495. 1884: Chem. Ind. 1884, p. 5. 1885: J. Soc. Chem. Ind. pp. 31 & 447; Berl. Ber. xviii. pp. 1376, 1384, 1391; J. Chem. Soc. xlvii. pp. 457 & 465. 1888: Berl. Ber. xxi. pp. 67 & 3223. 1889: Zeitsch. f. angew. Chemie, pp. 265 & 385. 1890: *ibid.* p. 195.

Of the different oxides of nitrogen, *nitrous oxide*, N_2O , need not detain us here. It is very slightly soluble in sulphuric acid, much less so than in pure water, as, once formed, it is not oxidized again into NO or higher nitrogen oxides; it is altogether lost for the manufacture of sulphuric acid, nor does it form any chemical compound with sulphuric acid.

Nitric oxide, NO, was said by Henry and Plisson to be absorbed by oil of vitriol, if left a long time in contact with it, with formation of nitrous pyrosulphuric anhydride (see below); but Berzelius, Gay-Lussac, and many others have long ago refuted this statement, more especially Winkler (*l. c.* p. 58). In fact the sulphuric acid of the absorbing-apparatus cannot retain that portion of the nitrogen oxides which has been reduced to the state of nitric oxide; and from this follows the necessity of an excess of oxygen in the gas issuing from the chambers, since only this prevents the existence of nitric oxide in the same. Small quantities of nitric oxide may, however, escape oxidation even in the presence of oxygen, and are hence found in the chamber-exit gases.

The solubility of NO in sulphuric acid, although not *nil*, is extremely slight, according to Lunge, J. Soc. Chem. Ind. 1885, p. 447 (1 c.c. of concentrated vitriol dissolves 0.000593 gram = 0.035 c.c. NO; dilute acid even less than this). This solubility is hence of no practical importance.

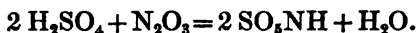
In the presence of oxygen nitric oxide is absorbed by sulphuric acid (Bussy, Winkler); but then it is really nitrous acid which is absorbed; and Winkler was the first to prove that it is precisely the presence of sulphuric acid which causes the oxidation not to proceed beyond the formation of nitrous acid, the latter combining afterwards with the sulphuric acid to form nitroso-sulphuric acid and water:—



In several of the above-quoted papers I have given strict proofs

of the same fact, viz., that on passing nitric oxide, together with a very large excess of free oxygen, through strong sulphuric acid, nothing but nitroso-sulphuric acid is formed, which means that 2NO take up only 1O ; but once out of the range of the acid, immediately above it, the reaction $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$ sets in, and this compound, when afterwards meeting sulphuric acid, yields equal molecules of nitric acid and of nitroso-sulphuric acid (*vide infra*).

Nitrous anhydride (*nitrogen trioxide*), N_2O_3 , dissolves in sulphuric acid, all the more easily when the latter is concentrated, but also, as we shall see, when it contains a certain amount of water. The reaction taking place is this:



Rammelsberg (*l. c.*) asserts that when nitrous anhydride is employed in excess, nitric acid and nitric oxide are also formed:



but this reaction only takes place in presence of water, and the formation of nitric acid and nitric oxide must be considered as a secondary reaction, owing to the well-known action of free nitrous acid on an excess of water. Where there is enough sulphuric acid and no excess of water, Rammelsberg's reaction does not come into play.

The compound formed by the action of nitrous acid on sulphuric acid of the empirical formula SO_5NH has long been known, both in the solid state, as "chamber crystals," and dissolved in an excess of sulphuric acid, as "nitrous vitriol"; but its true composition and nature has only comparatively recently been elucidated.

The easiest way of preparing the chamber-crystals in a state of purity is by conducting sulphur dioxide into well-cooled fuming nitric acid until the whole mass has been converted into a magma, but not until the nitric acid has been entirely decomposed, and drying the crystallized mass on a porous slab under a bell-jar over some oil of vitriol. Obtained in this way, or collected in the connecting-pipes of vitriol chambers or other places where there is a deficiency of steam, they consist of four-sided prisms or orthorhombic crystals; but generally, when prepared on the small scale, they appear as a scaly, feather-like, or granular mass, colourless and transparent. Their fusing-point is stated by Weltzien = 73° ,

by Gaultier de Claubry= 120° to 130° ; but they are partly decomposed before fusing, with evolution of red fumes.

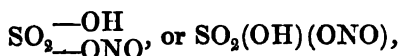
The composition of chamber-crystals was formerly uncertain; the question was, in the language of the older chemists, whether they were a compound of sulphuric acid with nitrogen peroxide, or with nitrous acid (nitrogen trioxide). Müller (Ann. Chem. Pharm. cxxii. p. 1) still pronounced for the former; but R. Weber proved in 1862, and more rigorously in the following year, by estimating all their constituents according to unexceptionable methods, that their formula must be constructed on the second supposition. His results were as follows:—

	Molecular weight.	Calculated.	Found.
2 SO ₃	160	62·39	64·00
N ₂ O ₃	76	29·92	27·96
H ₂ O	18	7·69	10·50
<hr/> 2 SO ₃ , N ₂ O ₃ , H ₂ O.....	<hr/> 254	<hr/> 100·00	<hr/> 102·46

This formula has also been confirmed by Michaelis and Schumann (*l. c.*), who at the same time maintained, from the products of decomposition by phosphorus perchloride, that the compound whose molecular weight has to be halved must be regarded as

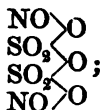
nitrosulphonic acid, $\text{SO}_2 \begin{smallmatrix} \text{OH} \\ \diagdown \\ \text{NO}_2 \end{smallmatrix}$ —that is, as sulphuric acid, one of

whose hydroxyls is replaced by the nitro group, or as nitric acid, for whose hydroxyl is substituted the sulpho group. This mode of explaining the constitution of that substance cannot, however, be strictly maintained. Both from its formation and the decomposition, it is certain that it does not contain the nitro group NO₂, but the nitroso group NO. Its formula must, therefore, be written:



and it must be called nitrosyl sulphate, or, most correctly, nitroso-sulphuric acid, which means sulphuric acid, one of whose hydrogen atoms is replaced by the nitroso group, that is, the radical of nitrous acid, NO(OH).

There exists also an anhydride of nitroso-sulphuric acid, of the empirical formula, $N_2O_3, 2SO_3$, which is rationally written :



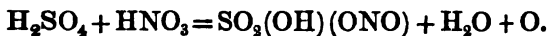
but this is only formed by mixing liquid sulphur dioxide and nitrogen tetroxide in the cold under pressure (Provostaye), or sulphuric anhydride with dry nitric oxide (H. Rose), or by heating sulphuric anhydride with nitrogen tetroxide (Weber), none of which reactions are possible in the manufacture of sulphuric acid.

Neither is this the case with the compound produced by R. Weber (Poggend. Annalen, clxii. p. 602) by conducting sulphuric anhydride into the most highly concentrated nitric acid, which has the empirical formula $N_2O_5, 4SO_3, 3H_2O$.

Nitroso-sulphuric acid is formed not merely in the above-indicated way, but in many other ways. We have already mentioned its formation from sulphur dioxide and nitric acid :



It is also formed when a mixture of strong sulphuric and nitric acids is heated, oxygen being evolved (A. Rose) :



On the other hand, sulphur dioxide can form that compound even with the lower oxides of nitrogen, if there is water and (except with N_2O_4 , where this is unnecessary) oxygen present. In the perfectly dry state sulphur dioxide does not act on the dry nitrogen oxides ; but in presence of the smallest quantity of water "chamber-crystals" are formed, if SO_2 meets with N_2O_4 , or with NO or N_2O_3 and oxygen. Winkler has shown that, in an atmosphere of moist carbon dioxide, nitrogen trioxide does not form chamber-crystals with sulphur dioxide, but nitrogen peroxide does so, and he distinguishes N_2O_3 and N_2O_4 in this manner. The fumes of N_2O_3 , with an excess of SO_2 and H_2O , but in the absence of oxygen, give no chamber-crystals at all ; they are decolorized, nitric oxide and sulphuric acid being formed. If oxygen or air are admitted, chamber-crystals instantly appear, and this is also the case when nitrogen peroxide meets sulphurous acid in the presence of water. These observations of Winkler's have been confirmed many times over.

As some points had not been entirely cleared up by the previous investigators, and there were partial contradictions among their results, I undertook a new investigation on the *interaction of sulphur dioxide and nitric oxide, with or without the presence of water* (Berl. Ber. xiv. p. 2196), which led to the following results :—

1. Dry NO and SO₂ have no action upon one another, be it at the ordinary temperature, or at 50° or at 100°, provided that air and moisture are rigorously excluded.

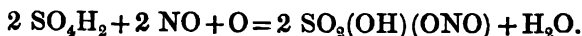
2. NO, SO₂, and water act in such a way that as much N₂O is formed as corresponds to the quantity of SO₂ originally present. A reduction down to N could not be established.

3. If NO and SO₂ meet in the presence of dilute sulphuric acid, of spec. grav. 1.455, no reduction of NO to N₂O takes place, even when there is a very large excess of SO₂ present, whether the digestion be carried on for many hours at ordinary temperature or at 60°. Even with acid of spec. grav. 1.32 no reduction of NO by SO₂ could be established.

4. If NO, SO₂ and oxygen meet in the presence of water, a slight but distinct reduction down to N₂O takes place. If, however, in lieu of water, dilute acid of spec. grav. 1.32 is employed, no such reduction can be observed.

The bearing of these results on the theory of the chamber-process will be discussed later on (Chapter IX.).

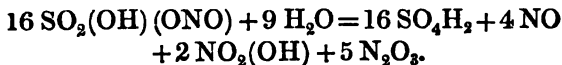
A further investigation by myself (Berl. Ber. xviii. p. 1384; Journ. Chem. Soc. xlvii. p. 465) confirmed the above results. It was shown that in the dry state nitric oxide combines with an excess of oxygen to form N₂O₄ exclusively, or nearly so; dry nitric oxide in excess with oxygen yields much N₂O₃ along with N₂O₄; in the presence of water, NO with an excess of oxygen is altogether converted into nitric acid. If, however, NO meets O in immediate contact with concentrated sulphuric acid, there is neither N₂O₄ nor HNO₃ formed, even with the greatest excess of oxygen; oxidation proceeds only to the stage of N₂O₃, which, however, is not formed in the free state, but passes into nitroso-sulphuric acid :



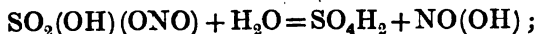
Outside the immediate contact with the acid the reaction is again as before with dry gases, viz. $2 \text{NO} + \text{O}_3 = \text{N}_2\text{O}_4$; that is, here NO is oxidized to a higher state than within the sulphuric acid.

A very elaborate investigation of the interaction between nitrous and sulphurous acid has been published by Raschig (Lieb. Ann. ccxli. pp. 161 *et seq.*). He has found a number of new compounds, and has rectified some of the statements of Frémy and Claus concerning compounds formerly described by them. He also discovered a very convenient method of preparing hydroxylamine. But as nearly all Raschig's experiments were made with alkaline solutions, and those which were made with acid solutions were made under conditions utterly different from those of a lead-chamber, viz. at the freezing-point, we cannot stop to give any details of his results. Under the just-mentioned circumstances, apart from N_2O and NO , amidosulphonic acid, hydroxylamine, and ammonia are observed, but only in small quantities; and above the low temperatures employed by Raschig the occurrence of those substances is altogether too uncertain and minimal to be taken into consideration for our purposes.

Action of water on chamber-crystals.—These are very deliquescent; they absorb water rapidly from ordinary air. In contact with a little more water, they dissolve quickly with evolution of heat, much nitric oxide being given off. When introduced into a large quantity of water, they dissolve without visible evolution of gas; but in point of fact nitric oxide is formed as well, also nitric acid, together with nitrous acid. This has led to many attempts at explanations, and Rammelsberg and Philipp have asserted that exactly $\frac{1}{4}$ of the nitrogen appears as NO , $\frac{2}{3}$ as nitrous acid, and $\frac{1}{3}$ as nitric acid:



But this complicated and very unlikely reaction need not be assumed at all. Every fact observed in this connection can be quite simply explained by the following reaction:



that is, nitroso-sulphuric acid takes up the elements of water, to form sulphuric acid and nitrous acid; the latter, as is well known, is unstable in the presence of any excess of water, and hence partly splits up into nitric oxide and nitric acid:



In the presence of less water, nitrous anhydride can be formed from chamber-crystals, and escapes in the shape of brown fumes :



For nearly every purpose nitroso-sulphuric acid or its solution in sulphuric acid may be looked at as a solution of nitrous acid in sulphuric acid.

The behaviour of nitroso-sulphuric acid towards sulphuric acid of various concentrations is of great interest for our purposes. In concentrated oil of vitriol the crystals dissolve easily and without decomposition. This solution is stable enough to be distilled without losing any nitrous acid, whilst the isolated crystals are decomposed on being gently heated. I have shown (Zeitsch. J. angew. Chemie, 1888, p. 661, and 1890, p. 447) that on distilling such a solution for four hours, when 40 per cent. of the sulphuric acid had passed over, the distillate contained only 5 per cent., the residue 95 per cent. of the nitrous acid, none of it having been destroyed. It is possible to obtain solutions of 1·9 sp. gr. ; they evolve with water nitric oxide, inflame phosphorus at 62° C., oxidize sulphur and many metals on distillation with evolution of NO; heated with ammonium sulphate to 160° they evolve nitrogen gas. Sulphur dioxide evolves nitric oxide; but a solution of nitroso-sulphuric acid in strong oil of vitriol (of 170° Tw.), even on long-continued treatment with dry sulphur dioxide, is only incompletely decomposed, and on addition of water still shows the presence of nitrous acid by the evolution of brown vapours. This explains the fact (well known to manufacturers) that *concentrated* vitriol contaminated by nitrous acid is only with difficulty purified by sulphurous acid. Heated, sulphurous acid decomposes chamber-crystals with evolution of nitrous oxide (Frémy). Further statements on the behaviour of sulphurous acid towards the solution of chamber-crystals in sulphuric acid, the so-called "nitrous vitriol," will be made when examining the process going on within the Glover tower. It is remarkable, and of great importance for the practice of sulphuric-acid making, that even dilute acids of 1·70 down to 1·55 sp. gr. dissolve the crystals in the cold without decomposition; the decomposition only commences when the specific gravity of the dilute acid has fallen below 1·55—that is, below the density of ordinary chamber-acid (Weber).

Nitrogen peroxide *, whether in the state of a liquid or a gas, strongly acts on sulphuric acids. If, according to Weber, nitrogen peroxide, made by gently heating fuming nitric acid (and therefore in any case not free from nitric acid), be added to sulphuric acid of different degrees of concentration, the following is observed:—The strongest oil of vitriol, down to 1·7 sp. gr., absorbs the nitrogen peroxide without coloration. Acid of 1·55 turns yellow; here the nitrogen peroxide is probably absorbed to a large extent similarly as by nitric acid, and no decomposition, as represented by the equation on page 154, has taken place, whilst this has to be assumed in the case of the stronger acids. Acid of 1·49 turns greenish yellow, of 1·41 intensely green; acid of 1·31 turns blue and evolves nitric oxide, which on applying a gentle heat escapes with violent effervescence. Weak acids are only coloured for a short time. From this may be inferred:—that acids of 1·8 to 1·7 combine with nitrogen peroxide with formation of nitroso-sulphuric acid; weaker acids simply absorb it; and the more dilute acids decompose it with formation of nitric oxide, nitrous acid, and nitric acid. The action of sulphurous acid on these mixtures is different according to their concentration. As mentioned above, the solution of chamber-crystals in concentrated vitriol is but incompletely decomposed even by a prolonged action of sulphurous acid; but the yellow mixture of 1·55 sp. gr. and the coloured more dilute acids are decomposed with strong effervescence of nitric oxide. It will be shown afterwards what part all these reactions play in the recovery of the nitrous gas in the manufacture, where the object is first to absorb the gas sulphuric acid of 1·7, and then again to liberate it from that solution.

Winkler gave a different account of the behaviour of liquid nitrogen peroxide from that of Weber. He states that it may be mixed with sulphuric acids down to 142° Tw., but that it

* We shall generally give this name to the compound formerly called "hyponitric acid" and now sometimes "nitrogen tetroxide" or "nitrogen dioxide." It is well known that in the gaseous state it consists of a mixture of molecules of NO_2 and N_2O_4 , of varying proportions, according to the temperature. At a low temperature, especially in the liquid state, it is $=\text{N}_2\text{O}_4$; above 180° $=\text{NO}_2$.

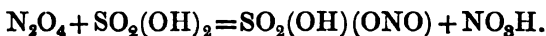
yields a solution totally different from that of chamber-crystals in sulphuric acid, viz. one of a yellow colour and constantly evolving red fumes. On heating, it effervesces and gives off streams of gaseous nitrogen peroxide; if the mixture was made with sulphuric acid of 142° Tw., the NO_2 completely volatilizes far below the boiling-point of sulphuric acid, so that the residue on dilution with water does not decolorize potassium permanganate. If, however, acid of 170° Tw. has been employed, the liquid on heating certainly yields up the larger portion of its NO_2 ; but the residue behaves like a solution of chamber-crystals in sulphuric acid, and on being mixed with water it evolves red fumes which can be proved to be N_2O_3 , not NO_2 , by their not forming any chamber-crystals with moist SO_2 .

There are some essential differences between the statements of Weber and those of Winkler, more especially so far as the behaviour of nitrogen peroxide is concerned, which had to be cleared up by further researches (see below).

If concentrated sulphuric acid is mixed with a little concentrated *nitric acid*, and sulphurous acid is passed into the mixture, the nitric acid in the cold is only reduced to nitrous acid, which remains combined with the sulphuric acid; this compound resists the further action of the sulphurous acid, similar to the solution prepared from concentrated oil of vitriol and chamber-crystals. On the other hand, more dilute mixtures of sulphuric and nitric acid, below 1.7 spec. grav., are more or less easily decomposed by SO_2 , in the ratio of their dilution.

Since the labours of Weber and Winkler did not in all points agree with one another, and the subject seemed to call for another investigation, I undertook a long research (Dingler's Journal, cccxxiii. p. 63), the conclusions of which (also published in the Berl. Ber. xii. p. 1058) are as follows:—

1. Nitrogen peroxide, under ordinary circumstances, cannot exist in contact with sulphuric acid, but at once splits up into nitrous acid, which, with a portion of the sulphuric acid, yields nitroso-sulphuric acid and nitric acid (dissolving as such), thus:—



2. Nitroso-sulphuric acid, on dissolving in an excess of sulphuric acid, forms a colourless liquid, but only up to a certain limit of saturation, which is so much the higher the more concentrated

the vitriol. This limit for vitriol of sp. gr. 1·84 is not yet reached $\pm 55\cdot34$ milligrammes $N_2O_3 = 185$ millig. SO_2 , OH, ONO in 1 cubic centim. of acid.

3. Beyond that limit at first a yellowish tint appears, of course with stronger acids only when more nitroso-sulphuric acid is present than with weaker acids. This took place with acid of sp. gr. 1·887 (made from pure vitriol of sp. gr. 1·84), containing in 1 cub. centim. 147 milligrammes $N_2O_3 = 372$ milligr. SO_2 OH, ONO, and also with acid of sp. gr. 1·706, containing in 1 cub. centim. only 56·7 milligr. $N_2O_3 = 190$ milligr. SO_2 OHNO₂. Since these acids also are rendered colourless by prolonged boiling, the excess of nitroso-sulphuric acid seems to be rather loosely held; but the temperature of the water-bath is not sufficient to affect it.

4. The phenomenon observed by Winkler, a mixture of strong vitriol and nitrogen peroxide showing an orange-colour even when cold, emitting red vapours, and exhibiting a tempestuous evolution of nitrogen peroxide on being gently heated (which proves the existence of unchanged nitrogen peroxide), can evidently take place only when the mixture contains *far* more N_2O_4 than the strongest mentioned above, or the strongest ever occurring in vitriol-works under any circumstances. Many experiments of heating in the water-bath for a prolonged period demonstrate with certainty the absence of free N_2O_4 in all cases observed. Still less can the presence of nitrogen peroxide be assumed in more dilute acids; it is therefore inadmissible to cite it as such in analyses.

5. All nitrous vitriols, *i. e.* solutions of nitroso-sulphuric acid in vitriol, whether they contain nitric acid at the same time or not, on being heated far below their boiling-point assume a golden yellow or even darker yellow colour, but entirely lose it again on cooling. This change of colours may be repeated any number of times. It hardly indicates a loosening of the combination, since this proves to be very stable even at much higher temperatures; but it may rather be compared to the deeper colour which ferric chloride solutions assume on being heated.

6. The stability of nitroso-sulphuric acid in its solution in sulphuric acid is very great, even at the boiling-point, providing the specific gravity is not below 1·70. It is true that on boiling some nitrogen is always lost, and all the more the less concentrated the acid is; but if the boiling takes place so that the vapour cannot condense and flow back, there is some nitroso-

sulphuric acid found in the residue, even from acid of sp. gr. 1·65 (comp. p. 152). But if the vapour is condensed and the condensing liquid (which, in the case of vitriol of sp. gr. 1·80 or below, consists of very dilute acid or almost pure water) is allowed to flow back, a considerable loss is caused by denitration.

7. Down to a concentration of sp. gr. 1·65 the affinity of sulphuric acid for nitrous acid, *i. e.* the tendency to the formation of nitroso-sulphuric acid, is so great that any nitric acid present at the same time, whether added as such or formed by the decomposition of nitrogen peroxide, is reduced with loss of oxygen, and employed to form nitroso-sulphuric acid. In the case of acid of sp. gr. 1·71 and upwards, this transformation takes place almost completely after a brief boiling, but at sp. gr. 1·65 only incompletely. This is a further argument against the existence of N_2O_4 in the solution.

8. Below sp. gr. 1·65 the nitroso-sulphuric acid possesses so little stability that, for instance, from acid of sp. gr. 1·60 some of it (but only a very small percentage) is expelled in the water-bath, and nearly all of it by boiling for a short time. In the case of acid of sp. gr. 1·5, it is evident that, even without heating, the nitrous acid added is partly decomposed into nitric acid and nitric oxide; but after heating for an hour in the water-bath, a considerable quantity of nitroso-sulphuric acid remains undecomposed, whilst another portion has been converted into sulphuric acid. In the case of still weaker acids, of course these phenomena occur even to a greater extent; but it is very probable that even very dilute sulphuric acid may contain, while cold, a little nitroso-sulphuric acid if reducing-agents are absent.

9. Most of the nitric acid present along with nitroso-sulphuric acid in dilute acids (of sp. gr. 1·5 and under) remains behind in the liquid even after prolonged boiling. If, therefore, the nitrous vitriol of acid-works, in consequence of a faulty process, contains nitric along with nitrous acid, it cannot possibly be completely denitrated by hot water or steam, in which case a less strength than sp. gr. 1·5 is never reached; the denitration can be only effected by reducing-agents, such as sulphurous acid in the Glover tower or mercury in the nitrometer. In the latter it can be very clearly seen with how much more difficulty and slowness the denitration goes on in the presence of nitric acid.

10. The tendency to form nitroso-sulphuric acid is so strong

that even if a large quantity of air (oxygen) is passed through sulphuric acid along with nitrous acid, no oxidation to N_2O_4 or N_2O_5 takes place, just as in the case of oxygen and NO.

11. Nitrous acid cannot be absorbed by caustic-soda solution without loss, because a portion of it is decomposed into nitric acid and nitric oxide.

12. The purple colour which is developed in nitrous vitriol by the action of reducing-agents, is caused by a solution of nitric oxide in such acids, and is possibly produced by a very unstable compound of nitrogen and oxygen, midway between NO and N_2O_3 .

Although my experiments had decidedly proved (comp. No. 1 and 4 of the just-quoted conclusions) that nitrogen peroxide does not dissolve as such in sulphuric acid, with formation of an unstable solution from which the N_2O_4 can be drawn off by heating, the former erroneous assertion of Winkler (since that time recognized as such by himself) did not vanish from chemical literature, and, for instance, gave rise to a decidedly erroneous explanation of the process of Lasne and Benker for treating the absorption in the Gay-Lussac tower. This caused me to investigate this matter once more (Berl. Ber. xv. p. 488). I pointed out that mixtures of pure nitrogen peroxide with even somewhat dilute sulphuric acid, down to spec. grav. 1.65, behave quantitatively as mixed solutions of equal molecules of nitroso-sulphuric acid and nitric acids; that on prolonged heating in a water-bath such solutions in acid of spec. grav. 1.75 lose nothing, and in acid of spec. grav. 1.65 only very little, of their nitrogen compounds. On prolonged boiling part of the latter escapes, but a large quantity of nitroso-sulphuric acid remains behind, more than that originally present, part of the nitric acid having passed into it with loss of oxygen. The idea of a "loose" union between N_2O_4 and sulphuric acid must therefore be entirely abandoned; and from this follows the fallacy of the idea held by some manufacturers that N_2O_4 was less easily absorbed by sulphuric acid than N_2O_5 , and that therefore much N_2O_4 was lost in the Gay-Lussac tower. I directly disproved this idea by showing that vapours of nitrogen peroxide were most easily, quickly, and completely absorbed by sulphuric acid of spec. grav. 1.71, such as is used in the Gay-Lussac tower, and that this (colourless) solution is not changed

either by long heating to 100° or by passing a current of air for a long time through it.

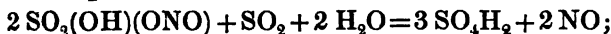
Sorel (Zeitsch. f. angew. Ch. 1889, p. 272) has made quantitative experiments on the *tension of nitrous acid in presence of dilute sulphuric acid at different temperatures*. He made a solution of pure N_2O_3 in concentrated sulphuric acid, entirely free from higher or lower oxides of nitrogen, and made it run slowly through a glass worm, of a width of $\frac{3}{8}$ inch and a total length of 16 feet, in such manner that the acid only wetted the glass walls, whilst a stream of dry nitrogen gas flowed in the opposite direction, and the nitrous acid carried away by it was absorbed in a dilute solution of potassium permanganate. The results are shown in the following table. The first column gives the strength of the sulphuric acid, the second the quantity of N_2O_3 dissolved (of course as nitroso-sulphuric acid), the third the temperature of the bath surrounding the worm, the fourth the quantity of N_2O_3 carried away by one litre of nitrogen, calculated at 0° C. and 760 millim. pressure.

Spec. grav. of sulph. acid at 23° C.	Grammes N_2O_3 per litre of acid.	1 litre of dry nitrogen carries away x milligr. N_2O_3 at the temperature t .	
		t .	x . mg.
1.824	142.0	37	0.079
1.791	28.4	41.4	0.009
"	"	61.2	0.049
1.774	28.4	40.1	0.009
"	"	62.1	0.095
"	"	89.7	0.274
1.745	25.876	29.5	0.044
"	"	61.4	0.196
"	"	75	0.402
"	"	88.9	0.980
1.672	4.734	29.5	0.29
"	"	46	0.37
"	"	75	1.29
"	4.500	58	0.54
"	4.640	90	2.72
1.666	9.403	45	2.69
"	7.730	65	9.59

Spec. grav. of sulph. acid at 23° C.	Grammes N ₂ O ₃ per litre of acid.	1 litre of dry nitrogen carries away <i>n</i> milligr. N ₂ O ₃ at the temperature <i>t</i> .	
		<i>t</i> .	<i>n</i> . mg.
1·642	14·652	28·1	2·00
„	„	42	4·58
„	„	63·4	21·73
„	„	75·8	56·58
1·624	9·995	90·1	36·44
„	10·795	89·9	40·39
1·606	11·558	91	64·38
1·603	1·259	70	4·90
1·601	2·500	40	0·94
„	2·216	65·2	7·29
1·597	1·792	90	11·77
„	12·500	89·9	109·15

These observations do not suffice for deriving a law from them ; but they distinctly show an increase of decomposition both with a dilution of the acid and with an increase of the temperature. Sorel also asserts that the amount of N₂O₃ retained by sulphuric acid must be a function of the tension of nitrous vapours in the atmosphere ; but he adduces no proof of this, nor is this quite likely, since (except with dilute acids) we certainly have not to deal with an ordinary solution, but with a chemical combination of nitrogen tetroxide. (An investigation on this subject, made in my own laboratory, will be found in the Appendix).

The behaviour of nitroso-sulphuric acid towards reducing reagents is of the greatest importance, both for the chamber-process in general and for the recovery of nitrogen compounds at the close of the system. The most important of the reagents in question is sulphurous acid, which acts as follows :—



that is, it forms with nitroso-sulphuric acid both sulphuric acid and nitric acid. This is the leading reaction of the Glover tower, as we shall see hereafter ; and it must also occur within the chambers, more especially in the first part of the set.

Sorel (Zeitsch. f. angew. Ch. 1889, p. 273) has shown that if a mixture of SO₂ and O is made to react upon nitrous sulphuric

acid and NO, there may be either a reduction of nitrous acid to NO, or an oxidation of NO to N_2O_3 (in the shape of SO_3NH), according to variations in the following conditions: temperature, dilution of the acid, proportion between SO_3 and O, percentage of NO. The extreme cases were well known before: a reduction takes place at high temperatures, with scarcity of oxygen and excess of water; an oxidation with excess of oxygen, concentrated acid, and low temperatures. For the intermediate cases Sorel has made some special experiments, from which it followed that in identical mixtures an increase of the temperature from $70^\circ C.$ to $80^\circ C.$ was sufficient to change the oxidation into reduction. At equal temperatures a reduction took place when the gaseous mixture contained 31 per cent. SO_2 , 10 per cent. O, 59 per cent. N, but an oxidation with a mixture of 21 SO_2 , 12.1 O, 66.9 N, &c. The reaction of SO_2 on nitrous sulphuric acid is nothing like so simple as previously assumed. If the acid exceeds the strength of 1.630, the SO_2 does not reduce the N_2O_3 to NO, but forms with it and sulphuric acid nitroso-sulphuric acid, so long as there is oxygen in excess and the atmosphere contains more N_2O_3 than corresponds to the tension of the acid in question at that special temperature (comp. above). Otherwise reduction to NO takes place. Acids below spec. grav. 1.600 are able to fix N_2O_3 under the same conditions, but only at comparatively low temperatures; at higher temperatures there is reduction even in the presence of an excess of O and N_2O_3 .

Another reducing agent whose action had formerly been overlooked is carbon, in the shape of the *coke* employed for packing the Gay-Lussac tower. I have shown (J. Soc. Chem. Ind. 1885 p. 31) that coke has a very strong reducing-action on nitric acid dissolved in sulphuric acid, which goes far towards explaining the fact that the "nitrous vitriol" from the Gay-Lussac towers never, except under altogether abnormal circumstances, contains any nitric acid, even when considerable quantities of N_2O_4 had been occurring in the exit gases. But the reduction goes further: some N_2O_3 itself, in the shape of nitroso-sulphuric acid, is by the coke reduced to lower nitrogen oxides and is thus lost. This has been proved by myself in my laboratory (Zeitsch. f. angew. Chem. 1890, p. 195); and as this is a matter of importance, we will give the results obtained in the following table:—

Material used.	Temperature. °C.	Time (hours).	Original percentage in N_2O_3 , grams.	Percentage decrease	
				in grms. N_2O_3 .	of the N_2O_3 originally present.
1. Nitrous Vitriol of spec. grav. 1·8375.					
Gas Coke in lumps	15	24	18·93	0·330	1·71
" "	14	2	18·92	0·539	2·86
" "	70	2	19·30	0·742	3·84
Oven Coke in lumps	15	24	19·30	0·285	1·48
" "	40	2	18·92	0·362	1·91
" "	70	2	19·30	0·452	2·34
Gas Coke in powder	15	24	19·30	0·790	4·09
" "	40	2	18·92	0·858	4·54
" "	70	2	16·22	0·903	5·57
" "	100	2	16·22	4·611	28·43
Oven Coke in powder ...	15	24	19·30	0·379	1·96
" "	40	2	18·92	0·451	2·38
" "	70	2	16·22	0·527	3·25
" "	100	2	16·22	2·770	17·08
2. Nitrous Vitriol of spec. grav. 1·725.					
Gas Coke in powder	15	24	19·50	0·333	1·98
" "	40	2	19·50	0·574	2·94
" "	70	2	19·50	0·891	4·57
" "	100	2	19·50	3·410	17·49

At 40° C., we see, two hours' contact reduced the percentage of N_2O_3 by 2·4 to 4·5 per cent.; at 70° the reduction sometimes went as far as 28 per cent. The latter temperature ought never to occur in a Gay-Lussac tower, but it does occur regularly in Glover towers up to the top. The conclusion is that coke packing ought to be entirely avoided in Glover towers, and that it is not advisable even for Gay-Lussac towers (comp. Chap. VIII.).

ANALYSIS OF SULPHURIC ACID.

Qualitatively sulphuric acid is always recognized best by the white precipitate of barium sulphide which it gives with barium chloride, both in the free state and in the solutions of its salts, even when very much diluted. This precipitate mostly settles down as a heavy powder, but in extremely dilute liquids occasionally appears only after some little time as a white cloud. Barium sulphate is as good as insoluble in water, solutions of salts, and free dilute acids; in concentrated acids it is a little soluble, especially on heating, also in concentrated sulphuric acid itself and in solutions of ferric chloride. On the other hand, in a very

concentrated liquid free from sulphuric acid, but containing much hydrochloric or, especially, nitric acid, the addition of barium chloride may cause a precipitate of barium chloride itself or of barium nitrate, which, however, is distinguished from barium sulphate by its crystalline appearance, and even more by vanishing on dilution of the liquid; barium seleniate is distinguished from barium sulphate by its solubility on boiling with concentrated muriatic acid, and by its behaviour with the blow-pipe. This reaction proves the presence of sulphuric acid either in its free state or in its salts; but of course it can no longer do this when the sulphuric acid has combined with organic substances to form "sulphonic acids," just because these contain neither sulphuric acid as such nor sulphates. In order to find sulphuric acid in the *free* state in the presence of sulphates of acid reaction, either the alcoholic solution of the substances can be tried with barium chloride (free acid being soluble, but all sulphates insoluble in absolute alcohol), or the charring properties of concentrated oil of vitriol are made use of by evaporating the solution mixed with a little cane-sugar in a small porcelain capsule on the water-bath, and observing whether a blackening of the sugar takes place. This reaction, however, also takes place with the sulphates of very weak bases, such as alumina or ferric oxide; nor can sulphuric acid be distinguished with certainty in this way from hydrochloric or nitric acid; but in phosphoric, acetic, tartaric acid, &c. a very small proportion of sulphuric acid can be proved by this reaction. The best reaction for free sulphuric acid, as well as for any strong free acid, is that with methyl-orange: this does not change its colour by metallic salts, but by the smallest quantity of free sulphuric acid.

In insoluble sulphates the acid is recognized by fusing them with alkaline carbonates, or by boiling with concentrated solutions of the same and filtering the solution of the alkaline sulphate formed thereby from the insoluble carbonates, or with the blowpipe, on charcoal, by the formation of sodium sulphate, according to well-known methods.

The quantitative estimation of free sulphuric acid for technical purposes is almost exclusively effected by volumetric methods or by the hydrometer. In both cases, of course, impurities will have a disturbing action; but for technical purposes they may nearly always be neglected (compare p. 126 *et seq.*). The hydrometric

estimation of sulphuric acid has been already described in detail; and we must here only point out again that the temperature must not be neglected in this case.

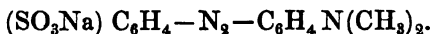
The volumetrical estimation of free acid generally takes place by means of a standard solution of potash, soda, or ammonia. According to the accuracy required, either a normal solution is used (that is, one containing per litre an equivalent expressed in grams), or a semi- or decinormal solution, &c. Some prefer ammonia, because it attracts but little carbonic acid, which makes the reaction with litmus less sharp; but its volatility is a drawback to ammonia solution, its smell proving a constant although minute loss. In dilute solutions (a stronger solution than seminormal ammonia ought never to be used) and in closed bottles this amounts to very little; but still it is not advisable to choose this liquid for very accurate work. As between caustic soda and caustic potash, Mohr prefers the latter, because the former sometimes cracks in the burettes. This is certainly true; but I have used a soda-burette cracked all over for a dozen years without any drawback.

As indicator formerly nearly always tincture of litmus was used, prepared by digesting litmus with six times its weight of water at the ordinary or a slightly higher temperature, pouring off the clear liquid, and filtering; sometimes a little spirit of wine is added to it. In order to obtain a sharp reaction, the solution, which is generally too alkaline, ought to be divided in halves: one half is stirred up with a glass rod dipped in dilute nitric acid, till its colour has changed from blue through purple into pure red; the other half is then added to it; and the purple mixture ought to be so sensitive that a quantity of pure water coloured strongly by it will be stained distinctly red by the least trace of an acid, and blue by a trace of alkali. The litmus-solution decomposes on keeping in closed vessels; it must therefore be kept in a loosely covered bottle.

Litmus is not well adapted for working in artificial light: the red appears almost as clear as water; the blue like a dark violet; but the transition from bright red into purple, &c., cannot be seen with certainty. This can be remedied by monochromatic light, if the artificial light be coloured yellow by common salt: the red appears clear as water, the blue like deep black; and the transition is even sharper than in daylight.

Litmus has, moreover, the disadvantage that it is sensitive to all weak acids as well, and that it is destroyed by sulphuretted hydrogen. If, therefore, carbonates are to be tested with it, this must be done at a boiling heat, and the boiling must be prolonged for some time. If any sulphides are present, an excess of acid must be added, all the H_2S must be expelled by prolonged boiling; only then the litmus must be added, and the analyses finished by re-titrating. This makes application of litmus very troublesome in alkalimetry; in fact a real error is introduced by the necessity of long boiling, if this is done in glass vessels which yield up some alkali thereby. In acidimetry this drawback is less felt, but only when the standard alkali is kept entirely free from carbonates, which is very difficult in the daily practice of alkali-works.

None of the drawbacks attached to the use of litmus apply to the indicator first proposed by myself*, viz., sulphobenzene-azodimethylaniline, formerly found in trade as a colouring-matter under the name of Poirrier's Orangé No. III., or Helianthine. Since it is now only used as an indicator, the name "methyl-orange," which I proposed, has become almost universally applied to it. It can be obtained from all dealers in chemicals, and is easily prepared by making a solution of 173 grms. sulphanilic acid in 15 litres of water, adding 120 grms. strong hydrochloric acid, slowly running in a solution of 70 grms. sodium nitrite in a litre of water (all being kept cool), and at last stirring in 121 grms. of dimethylaniline. The free acid thus formed and precipitated is best converted into the sodium salt:



This substance is dissolved in water, and a very small quantity of the solution is employed for each test. It is best to keep it in a bottle with a perforated cork, a glass tube drawn out to a point and inserted in the cork serving as a pipette for regulating the supply. Methyl-orange is orange in neutral solutions or in the presence of free alkali, but is faintly yellow in very dilute solutions, and no more ought to be added to the liquid to be tested

* In some places the introduction of methyl-orange is wrongly ascribed to W. von Miller, who proposed as indicator another colouring-matter called "Tropæoline OO," which has long since been abandoned as being far inferior to the above-named compound, about which comp. especially Chem. News, xlv. p. 288.

than suffices to colour it just perceptibly yellow. In this case the slightest excess of a *strong* acid will cause a very sharp transition into red, which is as delicate as *any* other indicator will permit. But when too much of the indicator has been added, so that the colour of the solution is orange, the transition into red (or, rather, in this case, into pink) is only gradual, and therefore useless. Warm solutions behave in a similar manner. It is therefore a distinct rule to be observed with methyl-orange, to employ as little as possible of it, and to work always at the ordinary temperature. This is made possible by the fact that methyl-orange is not acted upon by weak acids, such as CO_2 , H_2S , acetic acid, &c.; and this is undoubtedly one of its most valuable properties, since the trouble and loss of time in boiling the liquids, and the error introduced in the case of glass vessels, are thereby avoided. Both Na_2CO_3 and NaHCO_3 can be titrated directly in the cold just as well as NaOH , the total available soda being always indicated. Sulphurous acid behaves in the manner explained, *suprà* (p. 106), that is, the compound Na_2SO_3 is alkaline, NaHSO_3 neutral, to methyl-orange. Oxalic acid, as well as other strong organic acids, come in between sulphurous acid and the strong mineral acids; no sharp results can be got with them, and hence oxalic acid cannot serve as standard acid with methyl-orange. On the other hand, ammonia, which cannot be titrated with phenolphthalein, behaves perfectly normally towards methyl-orange, just like potash and soda. The normal sulphates of peroxide of iron, alumina, &c., which give an acid reaction with litmus, are neutral towards methyl-orange, so that any free acid present with them can be estimated by means of this indicator.

The tropæolines, formerly recommended as indicators, are nothing like so sensitive as methyl-orange, and are best not used at all as indicators, especially since several totally distinct compounds are comprised under this name, and the dealers do not always supply that which is really wanted.

Free sulphuric acid (including that contained in commercial ferric or aluminium sulphate, or any other sulphate) is estimated by adding a drop of methyl-orange solution, which causes a pink colour, and then adding a standard solution of alkali, till the pink tint has changed into pure light yellow. It is best to check this by reproducing the faint pink shade by means of a drop of standard acid.

The normal alkaline solution itself is best standardized by means of a normal acid, be it sulphuric or hydrochloric acid; and this on its part is best standardized by pure ignited sodium carbonate, which is easily obtained or prepared—for instance, by washing and igniting sodium bicarbonate. If sodium carbonate, bought as chemically pure, dissolves in water without any residue, and shows by the ordinary reagents no chloride or sulphate, or only unweighable traces of these, it can be used at once for standardizing normal acids after moderately igniting. If methyl-orange be used as indicator, this roundabout way need not be taken, but pure soda itself can be used as acidimetric liquid, either in a normal solution containing 53 grams per litre, or in more dilute solutions. The latter are more to be recommended, since the really normal solution causes efflorescences of sodium carbonate at the lower ends of the burettes, &c., which does not happen with semi-normal or weaker solutions, at least not for some time.

Although it is more important in alkalimetry than in acidimetry, we will here treat of the *standard acid* itself. As such many factory-chemists use sulphuric acid, but we recommend as more suitable hydrochloric acid, both because it can be used for estimating alkaline earths as well, and because it admits of a twofold way of checking the standard, either volumetrically by pure sodium carbonate, or gravimetrically by argentic nitrate. The gravimetric estimation of sulphuric acid by barium chloride is nothing like so accurate as the estimation of HCl in the shape of AgCl. Oxalic acid, most warmly recommended by Mohr, and consequently used by very many chemists, has great drawbacks. It is extremely difficult to prepare in the perfectly pure and dry state, without losing some of the water of crystallization; it does not keep in weak solutions, and it cannot be employed with methyl-orange. Oxalic acid is certainly very useful for other purposes than that of alkalimetry, namely, for testing Weldon mud, free lime in the presence of carbonates, &c. It is therefore indispensable in an alkali-works; but for acidimetry and alkalimetry sulphuric and especially hydrochloric acid are greatly to be preferred to it. Nitric acid might also be used; and it has this advantage in testing soda-liquors, that after neutralization by it the chlorides can be estimated in the liquid by silver nitrate, as will be explained when we describe the testing of soda-ash; but the metallic pinch-

cocks do not stand its use, and it requires special forms of burettes or glass cocks.

Since in a laboratory the normal acids frequently have to be restandardized, it is advisable to make a solution of exactly 26.5 grams of ignited sodium carbonate in a litre of water. This solution is kept in a stoppered bottle; and, for each testing, 10, 20, or 50 cub. centims. are taken out by means of a pipette, after shaking up the contents of the bottle in order to mix again any water evaporated and condensed in the upper part of the bottle. For the most accurate estimations it is always preferable to weigh each portion of sodium carbonate, directly after igniting and cooling, into the beaker, since it is never possible to measure as accurately as to weigh, because, among other reasons, the volumetrical apparatus very rarely agree quite accurately with one another. In spite of the trouble, it should most certainly not be neglected to compare, in the first instance, the pipettes with all the measuring-flasks, in order to see whether the former fill the latter precisely; secondly, to calibrate the burettes accurately, in which case it will often be found that the upper parts differ by several per cent. from the middle and lower ones, and cause a corresponding error. Of course the burettes must again be compared with the other measuring-apparatus. Lastly, the *measures* of the burettes, pipettes, &c. must be compared with the *weights* of water corresponding to them. In these tests the apparatus, even of first-class makers, often show large deviations, which may cause gross errors in analyses, and sometimes unpleasant disagreements with other analysts. But as to the *weights* from respectable makers, these are nearly always so near the truth that their deviations from it do not count in comparison with the unavoidable experimental errors; and they are, moreover, easily checked in the laboratory.

The standard acid is made to represent *equivalents*, not molecules; that is, if sulphuric or oxalic acid, it will contain one half of the molecular weight in grams, viz. 49 or 63 grams, because these acids are bivalent; but if the univalent muriatic or nitric acid, it will contain the total molecular weight, viz. 36.46 grams HCl, or 63 grams NO_3H . First of all, the acid is diluted a little less than necessary, and it is found out how many cub. centims. of it are required for a certain quantity of sodium carbonate. From this the quantity of water is computed which is required for obtaining an exactly normal acid; and after mixing this with the

acid the accuracy of the standard is ascertained by repeated titrating with sodium carbonate. Not less than 2 to 3 grams of the latter, or 100 cub. centims. of a semi-normal solution of it (26.5 grams per litre), should be taken for each test. If litmus is to be the indicator, to the alkaline solution drops of tincture of litmus are added till it becomes very markedly blue, then acid till strong effervescence sets in; and the liquid is now made to boil; then to the hot liquid gradually more and more acid is added, till the blue colour has passed through the purple and reddish purple of the CO_2 reaction to the bright red of the SO_4H_2 reaction. The liquid cooled by the addition of acid must be constantly heated again. Often, after several minutes' boiling, the apparently red liquid again turns purple and then blue. When working with boiling liquids there is never any doubt, to a single drop, upon the point where the pure red sets in. The test must be made in a porcelain capsule, not in a glass beaker. All this trouble is saved by employing methyl-orange as indicator and working in the cold.

When a perfectly accurate normal acid has been obtained, the normal alkali, whether ammonia, soda, or potash, is most easily made from it; and this is now used for the acidimetric test of sulphuric acid. Concentrated vitriol must, of course, first be diluted in the usual manner.

The analysis of fuming (Nordhausen) oil of vitriol, pyrosulphuric acid, and sulphuric anhydride will be described in the chapter treating of these substances.

The estimation of sulphuric acid in sulphates has been explained *supra*, when describing the assaying of pyrites (p. 53 *et seq.*).

The impurities of sulphuric acid are recognizable *qualitatively* in the following manner:—A *residue* on evaporating sulphuric acid in a platinum crucible may contain sulphates of sodium (more rarely of potassium), of calcium, aluminium, iron, lead; copper, zinc, or other metals occur rarely in sensible quantity. *Ammonium* sulphate is sometimes present in somewhat large quantities (Gintl, Chem. Zeit. 1879, p. 653). The individual substances are sought for by the ordinary analytical methods. *Iron* is already betrayed by the colour of the residue after ignition, and can also be detected in the acid itself, without evaporating it, by the ordinary reagents, such as potassium ferrocyanide, potassium sulphocyanide, &c. *Lead* is often shown as a white precipitate of sulphate on diluting concentrated vitriol with water—further, by adding one or two

drops of hydrochloric acid, by which white clouds are formed, which vanish on addition of more hydrochloric acid or on heating; with more certainty it is shown by diluting (even weaker acid) with three or four times its volume of strong alcohol. The precipitate must, of course, be examined further—for instance, with the blowpipe, by reduction on charcoal to metallic lead, by moistening with ammonium sulphide (which blackens it), &c.

Selenium is best found by adding a solution of ferrous sulphate or chloride; at the point of contact a red ring or cloud is produced, which increases by standing or heating, and ultimately the whole liquid is filled with red selenium, whilst the ring produced by nitric oxide vanishes on heating. *Arsenic* is recognized by sulphuretted hydrogen in a dilute solution, more safely by Reinsch's test—diluting with equal volumes of water and pure hydrochloric acid, and immersing a bright copper foil, which, after gentle heating, is covered with a fast-adhering slate-grey precipitate, which, according to Lippert, is a compound of copper and arsenic, Cu_3As_2 , (if the arsenic is present as arsenic acid, the reaction only sets in after longer heating); further, by Marsh's apparatus, in which, by means of pure zinc and water, the arsenic is given off as arseniuretted hydrogen, and is proved by reduction in a red-hot tube, or by lighting the gas and holding a piece of porcelain in the flame, on which any arsenic appears as spots. Since it is difficult to procure zinc absolutely free from arsenic, it is well to substitute aluminium foil for it. There may be arsenic acid as well as arsenious acid present; this can be proved by neutralizing with ammonia and adding magnesia mixture: any precipitate must contain the arsenic acid, the filtrate the arsenious acid.

Selmi (Gazz. chimica, x. p. 40) asserts that arsenic can be detected in acid which gives no reaction by Marsh's test, by adding to 1000 grams of the acid 300 grams water and some lead chloride, distilling and testing the first portions of the distillate with sulphuretted hydrogen.

Of volatile substances sulphuric acid may contain:—*hydrochloric acid* (from the common salt contained in the nitrate of soda), to be proved by nitrate of silver, after having diluted the acid, silver sulphate being also very little soluble; *hydrofluoric acid*, to be proved by heating in a platinum dish covered by a glass plate coated with wax and containing scratched-in figures; *sulphurous acid*, to be proved by the decolorization of a weakly blue solution

of iodized starch, or very accurately by reduction with zinc or aluminium to sulphuretted hydrogen, which is recognized by its turning lead paper brown or by colouring purple an alkaline solution of sodium nitroprusside (comp. p. 105 *et seq.*). The *oxygen compounds of nitrogen* are nearly always present in the sulphuric acid of trade. They are recognized in the simplest manner, and with nearly as much precision as by any other test, either by the decolorization of a drop of dilute solution of indigo on heating or by carefully pouring a solution of ferrous sulphate on the acid contained in a test-tube, so that the liquids do not get mixed. In the presence of traces of nitrous acids or of higher nitrogen oxides a brown ring will be formed at the point of contact; if more be present, the iron solution is coloured brown or black; but after some time it loses its colour again, especially if it has become warm by the reaction. *Selenium* also gives a red ring similar to that given by traces of nitrogen oxides; but the colour, instead of gradually going away, after standing for a time turns into a red precipitate at the bottom of the test-tube. Nitrous and hyponitric acids are also recognized by turning blue a solution of starch containing potassium iodide.

The most sensitive reagent for nitrogen acids is *diphenylamine*, which is most conveniently employed in a solution of 0.5 gm. in 100 c. c. concentrated sulphuric acid, diluted with about 20 c. c. of water. A few c. c. of this solution is poured into a test-tube or conical glass, and the solution to be tested is carefully poured on the top, so that the liquids mix only gradually. If traces of nitrogen acids are present, a splendid blue colour is produced at the point of contact. But as all other oxidizing substances, also selenious acid, produce that blue colour, errors may occur through the (very frequent) presence of selenium, which gives the blue reaction with diphenylamine even in the absence of any trace of nitrogen acids. It is therefore necessary to test first with ferrous sulphate, as described above, and if this reagent betrays the presence of selenium, a freshly-prepared solution of *brucine sulphate* may be employed, which produces a fine red colour with even the smallest traces of nitrogen acids, whilst it is unaffected by selenium (Lunge, Ber. d. deutsch. chem. Ges. 1887, p. 2031).

All the above-named reagents indicate both nitric and nitrous acid (the latter, of course, present in chemical combination as

nitroso-sulphuric acid, *vide supra*). It is, however, easy to prove the presence of the latter by itself, for instance by means of a mixture of starch solution with a solution of iodide of zinc (a blue colour being produced), and by means of various organic amines which with nitrous acid form corresponding azo-colours (Griess, Berl. Ber. xi. p. 624). Of these the most frequently used are: metaphenylene diamine, which produces a yellow colour with 0.1 milligrm. nitrous acid in a litre, or else a combination of sulphanilic acid and α -naphthylamine. I have shown (Zeitschr. f. angew. Chem. 1889, p. 666) that it is best to mix both substances, dissolved in dilute acetic acid, at once, and to keep this solution ready for use; any nitrous acid getting in from the laboratory air is thus betrayed from the outset by the reagent turning pink. This colour can be removed by shaking up with zinc dust and filtering. For actual use, the solution to be tested for nitrous acid is heated up to about 80°C ., and a few c. c. of the mixed reagent added to it, when a rose-colour will be developed with less than $\frac{1}{1000}$ mgr. N_2O_3 in one or two minutes. Solutions containing too much nitrous acid give only a yellow colour. In order to obtain a reagent which is not discoloured on keeping, a little of the α -naphthylamine is boiled with a few c. c. of water, the hot solution is poured off, and only this is used, mixing it with dilute acetic acid and a dilute solution of sulphanilic acid.

The *quantitative estimation of the impurities* contained in sulphuric acid is best carried out with various portions of the sample. Usually only the following are looked for. *Lead* is estimated by diluting the acids, if concentrated, with its own volume of water and twice the volume of absolute alcohol, when all of it is precipitated as PbSO_4 . *Iron* is estimated by reducing with pure zinc and titrating with potassium permanganate; not leaving out of sight its action upon SO_2 , N_2O_3 , &c. *Arsenic* is estimated by reducing any arsenic acid to arsenious acid by a stream of SO_2 , expelling this by CO_2 , and precipitating by H_2S . The presence of lead, antimony, copper, platinum, &c. makes this process very complicated (comp. thereon McCay, Amer. Chem. Journ. vii. no. 6). If the quantity of As is somewhat considerable, it can be reduced to As_2O_3 by SO_2 , followed by CO_2 ; the liquid is then neutralized by soda, and the As_2O_3 titrated by iodine solution (Kisling, Chem. Ind. 1886, p. 137).

The *volatile impurities* of sulphuric acid are estimated as follows:—

Sulphurous acid, if at all present in weighable quantities, can be estimated by a solution of iodine according to Bunsen's method. The *acids of nitrogen* (nitrous, hyponitric, and nitric) cannot easily be present along with sulphurous acid in sensible quantity; their quantity is very considerable, however, in certain intermediate manufacturing products ("nitrous vitriol"); and the methods for estimating it are therefore of great importance. Also in chamber-acid and in more concentrated products there is much oftener nitrous or even nitric acid present than sulphurous acid; and in this case the estimation of even small quantities is sometimes of importance, because they exert a very injurious action during the concentration of the acid in platinum.

So far as *nitric oxide*, NO, is concerned, Cl. Winkler has already proved that it is not absorbed by strong vitriol (Untersuchungen, 1867, p. 7). Kolb has also made experiments with acids of varying concentration (Bull. Soc. Indust. Mulh. 1872, p. 225), and has found that acid of 1·841 does not absorb even traces of NO; acid of 1·749 to 1·621 merely traces (2 to 6 milligrams to 100 grms. acid); acid of 1·426 absorbs 0·017 grm. NO; acid of 1·327, 0·020 grm. NO to 100 grms. My own experiments (Journ. Soc. Chem. Ind. 1885, p. 447, and 1886, p. 82; also Berl. Ber. 1885, p. 1391, and 1886, p. 111) show that concentrated O.V. absorbs per c. c. only 0·0000593 grm. = 0·035 c. c. NO, and acid of sp. grav. 1·500 only half that quantity—both being inappreciable in any ordinary mode of testing. In practice accordingly no account need be taken of nitric oxide, especially in the case of the stronger acids, since in any case it cannot be present in sufficient quantity for estimation; and the latter need only refer to the proper acids of nitrogen. Of these, again, only nitric and nitrous acid need be taken into account. Nitrogen peroxide, N₂O₄ (formerly called hyponitric acid), when dissolved in sulphuric acid behaves exactly like a mixture of equal molecules of nitric and nitrous acid. Nitrous acid itself does not exist in any but rather dilute sulphuric acid; in somewhat concentrated acid it exists as nitrosyl sulphate or nitroso-sulphonic acid, SO₂(OH)(ONO) (comp. above, p. 147 *et seq.*). The solution of this compound in sulphuric acid behaves, however, towards oxidizing agents and in most other respects exactly like a solution of nitrous acid, which,

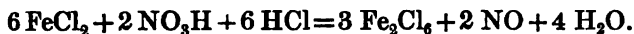
in fact, is formed from it by dilution with water. Ordinarily in doing this, part of the NO_2H is decomposed into NO and NO_2H (comp. p. 151), but this decomposition, which would interfere with the analysis, can be prevented by proper precautions, as we shall see below.

First of all we must treat of the methods for estimating *nitrous and nitric acids together*, in which case the result can be calculated as N_2O_3 , N_2O_5 , NO_2H , &c. Frequently, for technical purposes, it is calculated as NO_3Na , because the nitrate of soda is just the raw material whose consumption is the essential thing.

Of the many methods proposed for this end I only mention those which can be applied for technical purposes.

1. The method of *Pelouze*, modified by *Fresenius* and others, is only adapted for the estimation of nitric acid; it is, however, sometimes used for estimating a mixture of this and of nitrous acid, after the latter has been converted into nitric acid, for instance, by chlorine, potassium bichromate, permanganate, &c. Of course in the former case the excess of chlorine must be removed by boiling, which has always certain drawbacks, owing to the possibility of nitric acid being volatilized; in the two latter cases only an exactly sufficient quantity of the reagent must be added, which, especially in the case of permanganate, is easily ascertained by the change of colour.

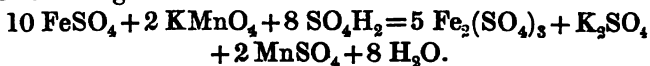
The method of *Pelouze* is founded upon the fact that free nitric acid oxidizes ferrous chloride or sulphate, according to the equation



By means of potassium permanganate the ferrous salt, not oxidized by nitric acid, is estimated, and the quantity of the latter is calculated from that of the ferrous salt consumed.

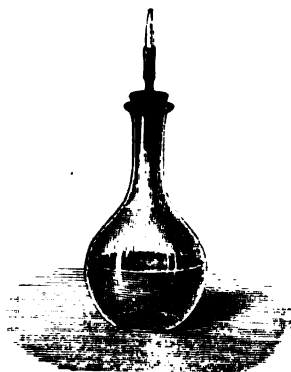
We shall describe the method here in a simple modification, which I have found just as efficient as the somewhat complicated process of *Fresenius*. A flask of about 200 cub. centims. (fig. 15) capacity is closed by a good cork or india-rubber stopper, through which a glass tube of about $1\frac{1}{4}$ inch length passes, cut off slanting just below the cork; its upper end is closed by a Bunsen's caoutchouc valve, viz. a piece of thick elastic tubing whose upper end is closed by a bit of solid glass rod, and which receives a sharp slit about $\frac{1}{2}$ inch in length. This slit allows any gas or vapour to get out, but not to get in, since its margins close all the more

tightly the more the air is rarefied within the flask; mostly the tubing in this case collapses. This simple contrivance does quite the same service as the retort with carbonic-acid apparatus &c. in Fresenius' plan. Into the flask an accurately weighed quantity of the finest iron wire (for instance that used for making artificial flowers) is put, say 1 grm., and pure dilute sulphuric acid is poured over it. It is preferable to throw 1 or 2 grms. of sodium bicarbonate into the flask just before putting in the cork, in order to expel the air by carbonic acid. Now the cork with its caoutchouc valve is put in, and the dissolution of the iron is promoted by gently heating; at last the liquid is boiled till it has become quite clear; then the lamp is taken away and the flask is allowed to cool, which may even be hastened by cold water. The valve prevents any air from entering the flask and oxidizing the ferrous sulphate; after cooling, such oxidation does not happen at all during the time the experiment lasts, if an excess of acid is present. The cork is then removed, the contents of the flask are diluted to about 200 cub. centims., and a solution of potassium permanganate added from a burette till the pink colour has just appeared, which can be seen best on a white ground. The value of the latter solution is found according to the following reaction:—



Here we must remember that the iron wire is not chemically pure iron, but only contains, according to Fresenius, 99.6 per cent. Fe; therefore either the corresponding quantity of wire, say 1.004 grm., must be weighed at once, or the figure found must be multiplied by 0.996. I have found such fine iron wire (flower wire) to contain as much as 99.9 per cent. of real Fe. I have shown (*Chem. News*, xxxvi. p. 145) that this apparatus permits quite sufficiently precise estimations of nitric acid to be made; but the operation takes a very long time, unless a large excess of acid is employed—for instance, 20 per cent. SO_4H_2 by weight of the

Fig. 15.



whole liquid. Otherwise the boiling must be continued till the liquid has attained this degree of concentration.

A solution of potassium permanganate is usually called semi-normal if it can give up half an equivalent of oxygen (O taken as=8) in milligrams per cub. centim.—that is, 0.004 grm. O. Such a solution is obtained by dissolving 15.82 grms. of pure crystallized potassium permanganate in a litre of water, and is very convenient for practical use; it must, however, be checked with iron wire as above described, since even the crystallized permanganate sold as “pure” often contains 1 to 2 per cent. of impurities, which, however, do not interfere with its stability. Each cub. centim. of this solution answers at the same time to 0.028 grm. metallic iron, or 0.139 crystallized ferrous sulphate, or 0.009 N_2O_5 , or 0.0105 NO_3H , or 0.01417 NO_3Na , or 0.00633 N_2O_3 (previously transformed into NO_3H). This solution changes so little even on prolonged standing, in well-closed bottles or burettes, that it is only necessary to check it about once every two months by a new experiment with metallic iron, or in some other way, *e. g.*, with oxalic acid, or with hydrogen peroxide in a “nitrometer.” It must be remembered that there is a source of error in employing permanganate in the presence of hydrochloric acid (compare Fresenius’ ‘Quantitative Analysis,’ 6th (German) edition, p. 281); but where, as in the present case, the employment of hydrochloric acid can be avoided altogether, this reason for avoiding the use of permanganate in titrating ceases to exist.

Instead of dissolving iron wire every time with the precautions above described (which for standardizing the permanganate is certainly indispensable), a solution of ferrous sulphate can very well be employed for estimations of nitric acid. It must contain so much free sulphuric acid that no further acid need be added in the subsequent operations; the presence of this free acid at the same time retards the oxidation of the iron solution so much that, at most, it need be tested for its strength only once a day. A solution of 100 grms. pure crystallized ferrous sulphate and 50 grms. of sulphuric acid in 1 litre of water is made; and for each testing a certain quantity, say 25 cub. centims., is taken out with a pipette. This is much more convenient than weighing off and dissolving iron wire on each occasion, and saves a great deal of time. First the value of 25 cub. centims. iron solution is determined by a seminormal permanganate solution, which itself

has been previously standardized by means of iron wire; this can be done in a few minutes. Then another 25 cub. centims. of the iron solution is put into the flask with caoutchouc valve; a certain quantity of the liquid containing nitric acid is added, then 1 to 2 grms. of sodium bicarbonate; the flask is closed with the valve cork, heated to boiling, and the liquid boiled for some time, till it has become perfectly clear and all nitric oxide is expelled; then it is cooled and titrated back with permanganate solution as described above. Now, of course, less will be used than for the first titration; and the difference indicates for each cub. centim. of the permanganate solution a quantity of 0.009 gram. N_2O_5 &c., as mentioned above in detail. Of course the quantity of liquid containing nitric acid must be so regulated that an excess of unoxidized ferrous sulphate is left. Sometimes the boiling must be continued for a long time, up to an hour, before all nitric oxide is expelled; in very dilute liquids a very large quantity of free sulphuric acid is needed to hasten the reaction.

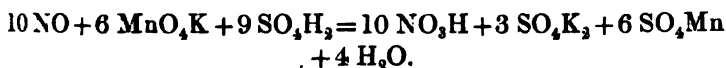
Another class of methods based upon the action of ferrous salts on the nitrogen acids is that first proposed by Schloesing, and subsequently modified by many others. In this class of methods the process is carried on in such manner that all nitrous and nitric acid present is converted into nitric oxide, NO , which is then estimated in various ways—mostly by measuring its volume as a gas. This method is very much used by agricultural chemists, especially in the modification introduced by Grandeau. A table for reducing the volumes of NO to weights of N_2O_5 for various temperatures and pressures has been calculated by Baumann (*Zeitschr. f. angew. Chem.* 1888, p. 662; reprinted in *Journ. Soc. Chem. Ind.* 1889, p. 135). For nitrous vitriol this method is seldom used, because it is far more troublesome than the nitro-metric methods to be described later on.

The iron methods, if carefully carried out, are very accurate; but they take some little time to complete, and the one first described has the drawback that the nitrous acid has first to be converted into nitric acid. The methods founded upon the reduction of nitrogen compounds to ammonia by nascent hydrogen require even far more time; they give accurate results only with special precautions, and are altogether far too troublesome for technical work, without offering any corresponding advantages in point of accuracy. We therefore refrain from any description of

these processes, as well as of those of Hasenbach, P. Hart, Crowder, Gerstenhöfer and others, employing urea, bleaching-powder, potassium bichromate, &c. (comp. the former edition of this work, vol. i. pp. 58-63). None of these processes seems to be in use, except perhaps here and there the bichromate process; but this also does not deserve attention in comparison with the two following, which are now almost universally employed.

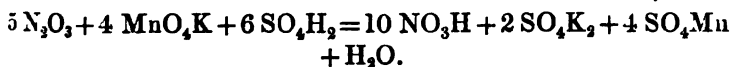
Among all the analytical methods founded upon the oxidation of nitrous acid, both the most convenient and the most accurate is that with *potassium permanganate*, first proposed by Feldhaus. Even for scientific purposes, there is no more accurate method for estimating nitrous acid in an acid solution than this, if other oxidizable bodies be absent.

Even nitric oxide is oxidized by this reagent, according to this equation:—



Accordingly the seminormal solution of permanganate, each cub. centim. of which corresponds to 0.004 O, will show 0.005 NO for each cub. centim. Thus, on the one hand, nitric oxide can be estimated quantitatively by this reagent; on the other hand, the nitric oxide would make the estimation of nitrous acid inaccurate if it were present at the same time, which, fortunately, is not the case in sulphuric acid to an appreciable extent.

Nitrous acid itself is oxidized by permanganate, according to the equation



Here every cub. centim. of seminormal permanganate solution corresponds to 0.0095 gram N_2O_3 .

The process formerly most in use was the following:—The nitrous vitriol was diluted to about 100 times its volume. Winkler asserted that this can be done without any loss of nitrogen compounds, if the nitrous vitriol be first mixed with three or four times its bulk of pure sulphuric acid, and the mixture be then carefully poured into cold water 100 or 200 times the volume of the nitrous vitriol, constantly agitating the liquid. Then permanganate is run in from a burette. It is at first decolorized

rapidly, then more slowly, as the oxidation of nitrous acid in very dilute liquids is not instantaneous. The end of the reaction is assumed if the pink colour has stood for two minutes. Later on, however, it bleaches out, owing to the presence of organic substances, which gradually act upon the permanganate.

I have shown that in this operation the figures obtained are always too low, and have directly proved the nitric acid formed in diluting the vitriol. Much better results are obtained by a modification which Professor Winkler has privately communicated to me, according to which 5 or 10 cub. centims. of nitrous vitriol are run out of a pipette on to the bottom of a beaker containing about 500 cub. centims. of water. The liquids are at first not mixed; and when the permanganate is added, the reaction principally takes place in the lower part of the liquid, where the nitrous vitriol is very little diluted. The results thus obtained are not quite accurate yet, but sufficiently so for ordinary factory work. Still simpler is the plan of running the vitriol into a small dry beaker, and pouring about three fourths of the requisite quantity of permanganate on the top of it. At the point of contact the nitrous acid is gradually oxidized as the vitriol gets diluted. After a few minutes the liquids are mixed by shaking, and quickly as much more permanganate is added as suffices for producing a pink colour.

The only safe plan is, however, that proposed by myself, namely, manipulating in the following way:—The permanganate is not run into the vitriol, but, on the contrary, a certain volume of permanganate solution is taken, and the nitrous vitriol is run in from a burette slowly, and with constant shaking, till the liquid is just decolorized. In the cold there is some loss of time, since the very dilute solution of permanganate is no longer acted upon instantaneously. This loss of time can be avoided by working at 30° to 40° C., but *no higher*. When working with concentrated sulphuric acid, this temperature is attained without any special means; otherwise the permanganate solution is heated up beforehand. If seminormal solution is employed, it is diluted with about 100 c. c. of tepid water. Sometimes a brown precipitate (of hydrated manganese peroxide) is formed in the operation; but this dissolves further on, and the final result is quite as correct in these as in any other cases.

In testing chamber acid, at most 5 c. c. of seminormal per-

manganate should be employed; otherwise the quantity of sulphuric acid required for decolorizing it will be inconveniently large. For proper "nitrous vitriol" from the Gay-Lussac tower up to 50 c. c. permanganate may be taken. If the number of c. c. of permanganate is called x , and that of the acid required for decolorizing it y , the quantity of N_2O_3 present in grams per litre of acid is $\frac{9.5 x}{y}$, calculated as

$$NO_3H = \frac{15.75 x}{y},$$

or as

$$NaNO_3 = \frac{21.25 x}{y}.$$

The following table saves the calculation in all cases in which $x=50$. The column y gives the number of cub. centims. of nitrous vitriol used, a the percentage in grams per litre, and b the percentage by weight for acid of $140^\circ Tw$. (For other strengths the percentage by weight is calculated by dividing the figures of column a by 10 times the specific gravity.) The figures in column a also indicate 0.01 lb. avoirdupois per gallon, or as nearly as possible ounces per cubic foot.

Table for estimating Nitrous Vitriol.

Acid consumed. y . c. c.	N_2O_3 .		NO_3H .		NO_3Na .	
	a . grms. per litre.	b . per cent.	a . grms. per litre.	b . per cent.	a . grms. per litre.	b . per cent.
10	47.5	2.80	78.8	4.62	106.2	6.22
11	43.2	2.54	71.6	4.20	96.5	5.65
12	39.6	2.33	65.7	3.85	88.5	5.18
13	36.5	2.15	60.6	3.55	81.7	4.78
14	34.0	2.00	56.2	3.28	75.9	4.44
15	31.7	1.86	52.5	3.07	70.8	4.14
16	29.5	1.74	49.3	2.89	66.4	3.91
17	27.9	1.64	46.3	2.71	62.5	3.65
18	26.4	1.55	43.7	2.56	59.0	3.45
19	25.0	1.47	41.5	2.43	55.9	3.27
20	23.7	1.38	39.3	2.30	53.1	3.11
21	22.6	1.33	37.5	2.19	50.6	2.96
22	21.6	1.27	35.7	2.09	48.3	2.82
23	20.6	1.21	34.2	2.00	46.3	2.71
24	19.8	1.17	32.8	1.92	44.4	2.60
25	19.0	1.12	31.5	1.84	42.5	2.49
26	18.3	1.08	30.3	1.77	40.8	2.39
27	17.6	1.03	29.1	1.71	39.4	2.30

Table for estimating Nitrous Vitriol (continued).

Acid consumed. y. c. c.	N_2O_5 .		NO_2H .		NO_2Na .	
	a. grms. per litre.	b. per cent.	a. grms. per litre.	b. per cent.	a. grms. per litre.	b. per cent.
28	17.0	1.00	28.1	1.64	38.0	2.22
29	16.4	0.96	27.1	1.58	36.7	2.15
30	15.8	0.93	26.3	1.54	35.5	2.08
31	15.3	0.90	25.5	1.49	34.3	2.01
32	14.8	0.87	24.6	1.44	33.3	1.95
33	14.4	0.85	23.9	1.40	32.3	1.89
34	13.9	0.82	23.2	1.36	31.3	1.84
35	13.6	0.80	22.5	1.32	30.4	1.78
36	13.2	0.78	21.9	1.28	29.5	1.73
37	12.8	0.75	21.3	1.25	28.7	1.68
38	12.5	0.73	20.7	1.21	28.0	1.64
39	12.2	0.72	20.2	1.18	27.3	1.60
40	11.9	0.70	19.7	1.15	26.6	1.56
41	11.6	0.68	19.2	1.12	25.9	1.52
42	11.3	0.66	18.8	1.10	25.3	1.48
43	11.0	0.65	18.3	1.07	24.7	1.45
44	10.8	0.63	17.9	1.05	24.2	1.42
45	10.6	0.62	17.5	1.02	23.6	1.38
46	10.4	0.61	17.1	1.00	23.1	1.35
47	10.1	0.59	16.8	0.98	22.6	1.32
48	9.9	0.58	16.4	0.96	22.2	1.30
49	9.7	0.57	16.1	0.97	21.7	1.27
50	9.5	0.56	15.8	0.925	21.3	1.25
55	8.6	0.50	14.4	0.835	19.3	1.13
60	7.9	0.46	13.1	0.765	17.7	1.04
65	7.3	0.43	12.1	0.705	16.4	0.96
70	6.8	0.40	11.2	0.655	15.2	0.89
75	6.3	0.37	10.5	0.615	14.15	0.827
80	5.9	0.35	9.85	0.575	13.3	0.778
85	5.6	0.33	9.2	0.538	12.5	0.730
90	5.3	0.31	8.7	0.510	11.8	0.692
95	5.0	0.29	8.3	0.485	11.2	0.655
100	4.7	0.28	7.9	0.462	10.6	0.620

In the presence of *other oxidizable substances*, such as sulphuric acid, ferrous salts, organic substances, &c., all oxidation methods are of course inexact, whether the bleaching-powder, or the bichromate, or the permanganate process. Generally those impurities are too insignificant to do any harm; and especially where large quantities of nitrous acid are present, as in the nitrous vitriol from the Gay-Lussac towers, the permanganate process is quite sufficient for the purpose of checking the course of manufacture. Of the oxidizable substances only arsenious acid sometimes occurs in sufficient quantities to affect the result.

sensibly, but to a small extent only, in nitrous vitriol, where it is mostly changed into arsenic acid.

The estimation of nitrous acid by means of aniline, which is converted into a diazobenzol salt, the end of the reaction being shown by potassium iodide and starch, has been practised for some time at several colour-works, long before it was published by Green and Rideal (J. Soc. Chem. Ind. 1886, p. 633). According to comparative tests made in my laboratory, it offers no advantage whatever over the very much less troublesome permanganate method.

From their very nature, as oxidation processes, all the just described methods indicate only that portion of the nitrogen acids which is present as nitrous acid. *Nitric* acid occurs much more rarely in sulphuric acid, but it may do so. Its presence may be recognized qualitatively by destroying all nitrous acid by means of urea, adding this up to the point where the reaction with iodide of zinc and starch ceases; any nitric acid present may now be proved by diphenylamine, brucine, or ferrous sulphate, &c. (comp. p. 170).

That process which is now mostly used for *the estimation of the total nitrogen acids* in sulphuric acids (as well as for that of nitrate of soda, comp. p. 78, of nitro-glycerine, and for many analogous purposes) is that discovered by Walter Crum (Phil. Mag. xxx. p. 426). It is founded on agitating the substance in question with mercury in presence of a large quantity of sulphuric acid, by which means all the nitrogen acids are converted into nitric oxide, NO, whose volume is ascertained by gasometric methods. Crum's process had been occasionally employed for the estimation of nitrates, *e. g.*, by Frankland and Armstrong, and had been specially recommended for nitrous vitriol by G. E. Davis (Chem. News, xxxvii. p. 45). But it had attracted very little attention, least of all with technical chemists, because it was cumbersome and expensive (requiring a mercury trough) and withal gave no very trustworthy results, owing to the difficulty of manipulation. I drew fresh attention to this process (Berl. Ber. xi. p. 436), and made it generally accessible, both by proving its accuracy under the circumstances here concerned, and by devising for it a special instrument, which made its manipulation extremely easy and simple. This instrument, which has since found a great variety of applications in gasometric and gas-volumetric analyses, some of which are mentioned in other parts of this work, has been called

the "*Nitrometer*." It is made in various shapes for various purposes; that shape which is used in testing nitrous vitriol is shown in fig. 16.*

Fig. 16.



* Since I first published my above-quoted paper, Campbell, Davis, and perhaps others have made known apparatus very similar to mine, for which they have adopted my name, "*Nitrometer*." Not one of these, however, combines all the advantages found in the instrument constructed by me.

Its principal portion is a glass tube, *a*, of a little over 50 cub. centims. capacity, divided into tenths of a cub. centim. At the bottom it tapers to fit an elastic joint; at the top it ends in a funnel *c* communicating with the inner part of the tube by a three-way tap. Its plug has one bore, through which the measuring-tube communicates with the funnel, and another bore through which the contents of the funnel can be run off. The division of the measuring-tube, *a*, begins from the tap itself, and goes from the top downwards. The tube *a* hangs in a clamp *e*, which can be instantaneously opened by a spring, so that the tube can be taken out. Another clamp *f*, sliding on the same stand, carries a plain cylindrical glass tube, *b*, tapering below, of the same contents and about the same diameter as the measuring-tube. The lower ends of the two tubes are connected by a thick elastic tube. *b* slides up and down in its clamp with friction. In order to use the apparatus, *b* is placed so that its lower end is rather higher than the tap *d*, and, the latter being opened, mercury is poured in through *b* till it has just come up to the funnel *c*. As it flows into *a* from below, it will not allow any air-bubbles to remain in the tube. The tap *d* is now closed; *b* is lowered; and the vitriol to be tested is run into the funnel *c* by means of a fine pipette. Of course it is necessary to have an idea of the maximum quantity of NO which may be given off without expelling the mercury from the tube altogether; and the quantity of vitriol must be taken accordingly. By carefully opening the tap *d*, the acid is run into *a* without any air being allowed to enter; in a similar way the funnel *c* is washed out twice by means of pure concentrated sulphuric acid. It is not advisable to put more than 8 to 10 cub. centims. of acid into the apparatus; much better only 4 to 5 cub. centims. altogether are used; but in any case there must be an excess of strong sulphuric acid present. Now the tube *a* is taken out of the spring clamp and well shaken up. The evolution of gas in the case of nitrous acid commences at once—the acid taking a purple colour, in the case of nitric acid, after a minute or so. The reaction is ended by one or two minutes' violent shaking. Sometimes it takes a good while before the acid clears and the froth subsides; but mostly this is the case in a very short time; and anyhow it is necessary to wait a little, so that the apparatus may take the temperature of the air. Now by sliding *b* up or down, the level of the mercury in this tube is so placed that it is

as much higher than that of *a* as corresponds to the vitriol; say, for each 7 millims. of acid 1 millim. of mercury; or else the level of the mercury is made the same in both tubes, and the height of mercury corresponding to the layer of vitriol in the tube is deducted from the barometrical pressure. In the former case it is easy to ascertain after reading off whether the proper compensation for the height of the acid column has been made or not. It is only necessary to cautiously open the tap *d*, over which a drop of acid has been left standing. If this is sucked in, and the level of the acid falls, there has been too little pressure, and *vice versa*. The volume of the nitric oxide can be read off to $\frac{1}{20}$ cub. centim.; it is reduced to 0° and 760 millims. mercurial pressure, and the percentage of the acid calculated from it. Each cub. centim. of NO, measured at 0° and 760 millims., corresponds to 1.343 milligr. NO, or 1.701 milligr. N_2O_3 , or 2.417 milligrs. N_2O_5 , or 4.521 milligrs. NO_3K , or 3.805 NO_3Na . By this process, of course, nitric and nitrous acids cannot be distinguished, but are always estimated together.

After reading off, *b* is again placed higher, the tap *d* is opened so that tube *a* communicates with the small outlet tube, and thus first the nitric oxide and then the vitriol, muddy with mercuric sulphate, is driven out. When the mercury begins to run out as well, the tap is closed, and every thing is ready again for a new testing. If any sensible quantities of sulphuric acid be present (as proved by the smell), it is best to add a very little powdered potassium permanganate to the vitriol, avoiding any considerable excess.

The nitrometer was first provided with a three-way tap on Cl. Winkler's principle, with one tranverse and one longitudinal bore; but now another arrangement, known as the "Greiner-Friedrichs" or the "Geissler-Miescher" tap, and shown in the diagram, is preferred, which admits of much easier manipulation and is much less liable to leakage.

It has been stated by T. Bayley that it is necessary to dilute the acid contained in the nitrometer at the close of the experiment, in order to expel the nitric oxide dissolved by the sulphuric acid, and that otherwise an error of about 0.5 c. c. is committed. I have proved this to be entirely wrong, no measurable quantity of NO being dissolved by the acid contained in the nitrometer (J. Soc. Chem. Ind. 1885, p. 447, and 1886, p. 82). This

could not be contradicted by Mr. Bayley, who, however, contended that the iron contained in the acid as ferrous sulphate acted as solvent for NO. I replied to this (Chem. News, 1886, liii. p. 289) that the quantity of iron found in any commercial acid would never lead to any appreciable error of this kind, all the more as it would be present as ferric sulphate.

From the volume of NO read off, and reduced to 0° C. and 760 mm., the nitrogen compounds present are calculated by the following table, in which column *a* gives milligrams, and *b* per cent. by weight, when employing in the nitrometer 1 c. c. acid of 140° Tw.

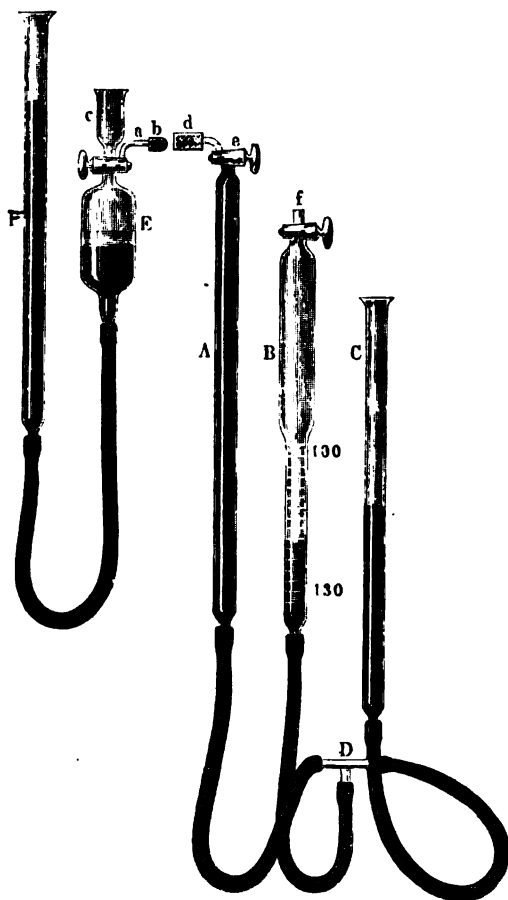
c. c. NO.	N.		NO.		N ₂ O ₃ .		NO ₂ H.		NO ₂ Na.	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
1.	0.627	0.0366	1.343	0.0785	1.701	0.0995	2.820	0.1648	3.805	0.2225
2.	1.254	0.0732	2.686	0.1570	3.402	0.1990	5.640	0.3296	7.610	0.4450
3.	1.881	0.1098	4.029	0.2355	5.103	0.2685	8.460	0.4944	11.415	0.6675
4.	2.508	0.1464	5.372	0.3140	6.804	0.3580	11.280	0.6592	15.220	0.8900
5.	3.135	0.1830	6.715	0.3925	8.506	0.4975	14.100	0.8240	19.025	1.1125
6.	3.762	0.2196	8.058	0.4710	10.206	0.5970	16.920	0.9888	22.830	1.3350
7.	4.389	0.2562	9.401	0.5495	11.907	0.6965	19.740	1.1536	26.635	1.5575
8.	5.016	0.2928	10.744	0.6280	13.608	0.7960	22.560	1.3184	30.440	1.7800
9.	5.643	0.3294	12.087	0.7065	15.309	0.8955	25.380	1.4832	34.245	2.0025

In spite of the very great convenience and speed and accuracy of the nitrometric estimation of the nitrogen acids, many chemists would have abstained from using it because the unavoidable reduction of the volume of NO to 0° C. and 760 millim. pressure would appear too tedious to them. In order to overcome this objection I have calculated tables which admit of reducing any volume of gas from 1 to 100 from any given temperature to 0° C., and from any given pressure to 760 millim., by simple reading off. These tables were given in the Appendix to my first edition; they are also contained in Lunge and Hurter's 'Alkali-Maker's Pocket-book.' Other tables, requiring very little more time for use, are found in Winkler-Lunge's 'Handbook of Gas-Analysis,' p. 115, *et seq.*

I abstain here from giving these or any other tables, as an instrument invented by myself, and called the "gasvolumeter" (Zeitschr. f. angew. Chem. 1890, p. 139; Berliner Berichte, 1890, p. 440), has made unnecessary all and any calculations and tables in connection with the reduction of volumes of gases to 0° and 760

millim. This instrument, as shown in fig. 17, consists of three glass tubes, all joined by very strong elastic tubes to a three-way pipe D, and sliding upwards or downwards in strong clips. Tube A is the measuring-tube, B the reduction-tube, C the level-tube. A is divided into tenths of cub. cent. and generally holds 50 c. c. ;

Fig. 17.



where larger volumes of gases are to be measured it is shaped like B, and measures 60 or 100 c. c. in the upper, wider portion, and another 40 c. c. divided in $\frac{1}{10}$ c. c. in the lower, narrower portion. The "reduction-tube" B holds 100 c. c. in the upper part, and

another 30 c. c., divided in $\frac{1}{10}$, in the lower part. This tube is set once for all in the following way. After putting the apparatus together and partly filling it with mercury, the temperature close by B and the barometric pressure are taken, and it is calculated, by the well-known formula

$$\frac{(273 + t)760}{273 \times b}$$

(where t means the temperature in 0°C. , b the height of the barometer in millimetres), what would be the volume of 100 c. c. dry air under the then atmospheric conditions. (This calculation can be abridged by using any of the above-mentioned tables, if they are at hand.) Suppose $t=20^{\circ}$, $b=750$ millim. In this case 100 c. c. of dry air would occupy the volume 108.8 c. c. We now move B and C so that, tap f being open, the level of the mercury in B is at 108.8, whilst the mercury in C is, of course, at the same level. Previously to this we have introduced a drop of strong sulphuric acid into B, but not sufficient to reach over the meniscus of the quicksilver, which would be an impediment to taking the readings; this is done, because afterwards gases have to be measured in the *dry* state. (In the more frequent case in which this instrument is employed for measuring *moist* gases, in lieu of sulphuric acid, a drop of water is introduced into B, and the calculation is made by deducting from the barometric pressure the tension of aqueous vapour corresponding to the existing temperature.) Now tap f is closed, and is secured in such manner that no air can enter or escape through it. In lieu of this tap a capillary tube may be provided which is sealed by a small flame, after having put a perforated piece of asbestos cardboard over the top of tube B, to prevent its temperature rising during the sealing-operation. (The dealers in scientific apparatus supply tubes sealed at both ends, and containing a volume of air corresponding to exactly 100 c. c. at 0° and 760 millim. together with some mercury. These tubes are put into the corresponding elastic tubes previously filled with mercury, and the lower capillary is broken by a pair of nippers through the elastic tube, whereupon the instrument is at once ready for work. Where there is a barometer for the first setting of the tube, it is, of course, preferable to do this one's self.)

It is quite evident that every time the level-tube C is raised so far that the mercury in B rises to the point 100, the air within B is compressed to the volume it would occupy at 0° and 760 millim.

independent of the temperature and barometric pressure actually existing. Now suppose we have evolved or carried over into tube A a certain volume of gas, and we adjust the position of the three tubes so that the mercury in B stands at 100° , and that in A exactly at the same level as in B, it is evident that the gas in A is under the same pressure as in B, and, supposing its temperature to be the same (which will be the case if these two tubes are close together), the gas in A will be equally compressed as that in B to the volume it would occupy at 0° and 760 millim. barometric pressure. The reading taken in A thus yields at once the corrected volume without having to look at a thermometer or barometer, or using any calculations or tables.

Tube A might be an ordinary nitrometer; but it is far preferable to use it only as a measuring-tube, and thus to keep it always clean and dry, whilst the nitrometric operation proper is carried out in the auxiliary apparatus EF. E is a non-graduated vessel, holding 100 to 150 c. c., and connected by a strong elastic tube with the level-tube F. The vessel E bears at the top the usual three-way tap and cup *c*. The side-tube *a* can be closed by a small ground-on cap *b*, or else an india-rubber cap. Before commencing the analytical operation, the tube F is raised so that the mercury just issues out of *a*; cap *b* is now put on and tap *c* is closed. Now the nitrous vitriol (or solution of nitrate of soda, comp. p. 78) is introduced through *c*, by carefully lowering F, so that only the liquid, but no air, enters into E; strong sulphuric acid follows, to rinse out cup *c*; the tap is now entirely closed, and E is violently shaken till the decomposition is complete and no more NO is given off. The cap *b* prevents the mercury in tube *a* from being thrown out in the shaking. The instrument is allowed to cool down, and is then put in the position shown in the diagram, so that the small tubes *a* and *d* are on the same level. Previously a short piece of india-rubber tube has been slipped over *d*, and by raising C the mercury has been forced right to the end of *d*. Now cap *b* is taken off, and *a* is introduced into the short elastic tube, till the glass tubes *a* and *d* touch. Now tube C is lowered and F raised (as shown in the diagram), and tap *c* is cautiously opened (*e* having been left open before). The gas will thus be transferred from E into A; in the moment when the sulphuric acid has entered into the bore of *e*, but before it has got inside of A, tap *e* is closed. Now the reading is taken as described

above; the apparatus EF may be detached at any time and cleaned as occasion arises.

The readings of the volume of NO, taken in tube A, may be converted into grams of N_2O_3 or $NaNO_3$, &c., according to the table given on p. 185. If nitrate of soda has to be analysed, each c. c. will indicate 3.805 millig. $NaNO_3$; hence, if 0.3805 gram of nitrate were employed for the test, the number of c. c. of NO would at once indicate the percentage of $NaNO_3$. In the case of nitrous vitriol the quantity will be usually not weighed, but measured by means of a pipette, and the results obtained must then be divided by the specific gravity of the acid to reduce them to weight percentage. If the acid is near 140° Tw., this is unnecessary; for in this case a 1 c. c. pipette will deliver 1.70 gram acid, and as each c. c. of NO indicates 0.0017 N_2O_3 , this means that the number of c. c. read off is exactly = tenths of a per cent. of N_2O_3 by weight of the nitrous vitriol.

CHAPTER IV.

THE PRODUCTION OF SULPHUROUS ACID.

A. BRIMSTONE-BURNERS.

ALREADY in the historical part attention has been drawn to the point that important progress was made in the manufacture of sulphuric acid when the *periodical* combustion of sulphur *within* the acid-chambers was replaced by *continuous* work in *special apparatus attached to the chambers*. This led to making the sulphur-burners altogether independent of the chambers, and conveying the gas generated in the former by a flue into the latter.

Whilst in the old periodical style of working only the oxygen actually present in the chamber could come into play, and therefore after every combustion the chamber had to be supplied with fresh air by opening the door and a special valve, of course at the expense of much inconvenience and loss of gas, in the continuous style of work the necessary air constantly enters the burner by suitable openings at the same rate as the products of combustion are aspirated into the chamber by the draught prevailing throughout the apparatus. The continuity of work must be further aided by employing a combination of several burners, so that there shall always be burning sulphur present. There are also burners to which the brimstone is continuously supplied, in order to avoid the drawback of irregular supply of air and gas occurring even with the combination of several ordinary burners.

The plainest sulphur-burners, such as were the most usual in England, are represented in figs. 18 to 20.

The burner consists of a brick chamber covered by an arch, the bottom being formed by a cast-iron plate, *a*, separately shown in fig. 20. This plate at the two long sides and one of the ends has a somewhat slanting-up flange of 3 inches height—in front, however, only 1 inch, so as to get out the ashes more easily. The

Fig. 18.

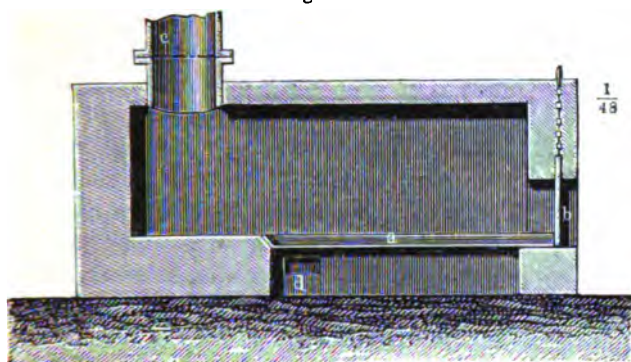


Fig. 19.



Fig. 20.

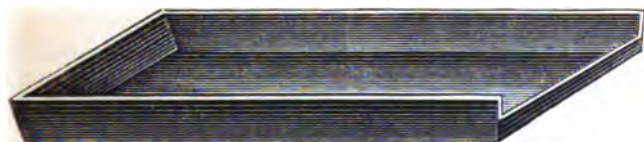


plate does not go right through the burner, but leaves the last third of it free ; in this part of the chamber the sulphur vapour, which is always formed, can mix with the excess of air and be burned. Rarely, however, this is completely performed, and there is generally some sulphur carried away unburned. This not only causes a loss, but also easily leads to the chamber-acid getting muddy and being covered by a thin membrane of sublimed sulphur, which prevents the contact between the bottom acid and the gas, very necessary for the chamber process. The burner is further

provided with an iron door, *b*, sliding in a frame and adjustable by a chain and balance-weight; also with a pipe, *c*, for taking away the gas. An air-channel, *d*, below the plate is in connection with a small chimney, or sometimes only with the open air, in order to cool the metal plate to some extent and prevent the sublimation of sulphur. There are always several furnaces of the kind combined together; each of them, with plates of 8 feet x feet, can burn 5 cwt. of brimstone in 24 hours, which is put in 6 portions, one every 4 hours; if four furnaces are combined, one of them is charged every hour. Sometimes, however, much larger and more frequent charges are made (see below). In these burners usually at the same time the nitric acid is liberated by placing cast iron pots, provided with three feet and containing a mixture of nitre and vitriol, amidst the burning sulphur by means of large tongs.

For a start the plates are heated by a small fire of wood shavings, the door being left open, not till the iron becomes red hot, but only till the first charge of sulphur ignites of its own accord or can be easily lighted by a red-hot iron; the further charges always find the burner sufficiently warm. A special fire-grate below the plate, to be used only at the start, is sometimes provided, but is quite unnecessary. The admission of air is regulated by opening the door, *b*, more or less widely; and its position is fixed by putting a wedge underneath the door, or by hooking the balance-chain to a nail driven into the brickwork outside. In the beginning, when the chambers are filled with air, the damper in the draught-tube is only opened gradually, to chase the air away more thoroughly.

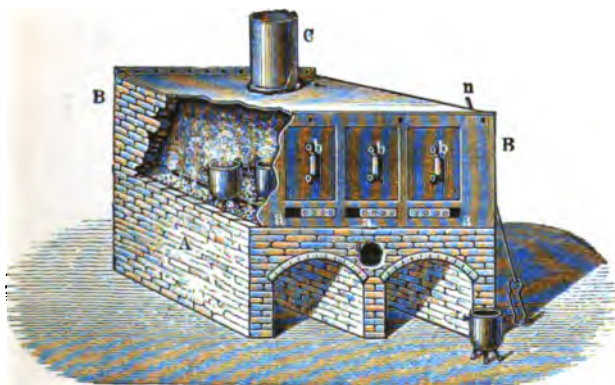
The style of working is generally rather rough; it must be considered that such burners are now-a-days hardly found in large works, where more supervision can take place. Before the attendant pulls up the door, he convinces himself of the state of the chambers so as to judge how much nitre he is to "pot" along with the brimstone. Often the nitre is merely measured by guesswork. First the brimstone is thrown in; the door is immediately let down, then a sufficient quantity of chamber-acid is poured into the nitre-pots, always by guesswork; the door is opened again, and the pots are placed among the brimstone, now already on fire, by means of an iron fork made for the purpose. The heat produced by the progress of the combustion drives off the nitric acid, and this enters the chambers along with the sulphurous acid.

When the time is up, the door is raised again, and the ashes are raked out; first, however, the nitre-pots are lifted out and emptied of their liquid contents. Then a new charge is made as above, and so forth. In all other sulphur-burners, excepting the continuous ones, the work is carried on in the same way; only the introduction of the nitre sometimes takes place in a less rough way, or nitric acid is used directly in the chambers.

It is a sign that the burner is working well if the brimstone burns with a pure blue flame; as soon as the flame takes a brown tinge, it is a sign that much sulphur is subliming, and care must then be taken to cool the plate by the flue underneath.

A somewhat more perfect apparatus is shown in fig. 21. A is

Fig. 21.

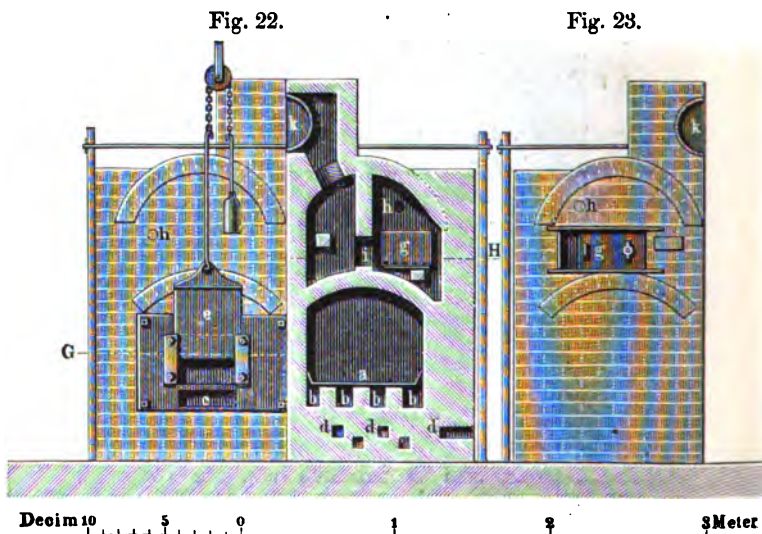


the foundation, B the chamber for burning the sulphur, C the gas-pipe. The foundation carries a cast-iron plate which covers the whole furnace-bottom, and is inclined a little forward. The combustion-chambers are at the sides bounded by brick walls, but in front, at the back, and at the top by cast-iron plates; in front also are the charging-doors, *b b*, and small openings, *a a*, provided with slides for regulating the access of air. The furnace-bottom is divided by 3- or 4-inch iron bars into three compartments, corresponding to the doors and draught-holes, which are served by turns. Inside the pots are visible, into which the mixture of nitre and vitriol is charged. The details of construction are often very different from those shown in the diagram; there are burners with more or fewer working compartments, with different regulation of air, with rails over the bottom plates for pushing in

a box instead of the nitre-pots, &c. The nitre-pots must receive a very small charge; otherwise the danger of boiling over is considerable, and the sodium sulphate among the brimstone is very troublesome. When nitric acid is used in the chambers, the nitre-pots are not wanted at all.

Sometimes the iron sides of the sulphur-burners are made double, and an air-channel is left in the space between; thus, of course, the temperature of the burner can be regulated to a nicety by opening up a draught through the double iron wall when the burner gets too hot, and shutting up the draught when it gets too cold.

The diagrams figs. 22 to 25 show a set of two burners free from most of the drawbacks mentioned. Fig. 25 is a sectional plan taken at two different levels; fig. 24 a longitudinal section; fig. 22 half front elevation, half cross section; fig. 23 back elevation.



a is the cast-iron bottom plate for burning the sulphur; it is carried hollow on pillars; and the channels *b b* formed thereby underneath the plate communicate with the outer air by the opening *c*, so that the plate can be cooled from below. The channels, *d d*, left in the foundation a little further below, communicate with this system, and ultimately end outside at *d'*. Owing to the difference of level and temperature, the air must always enter at *d'* and get out at *c*; its quantity can be easily regulated by partially closing *c*. The door, *e*, is hung in the usual way. The gas of the

burner does not go straight to the chamber, but first ascends through the opening *f* into a space separated from the burner proper by an arch. Just above the opening there is a grating, on which the nitre-pots are put, being introduced by the door *g*. There is here a small hole, *h*, lined with an iron tube, for admitting a little more air to the upper compartment and burning any sublimed sulphur. The gas first returns to the front, then back again through the hole *i* and the second half of the upper compartment, and at last escapes through the cast-iron pipe, *k*, common

Fig. 24.

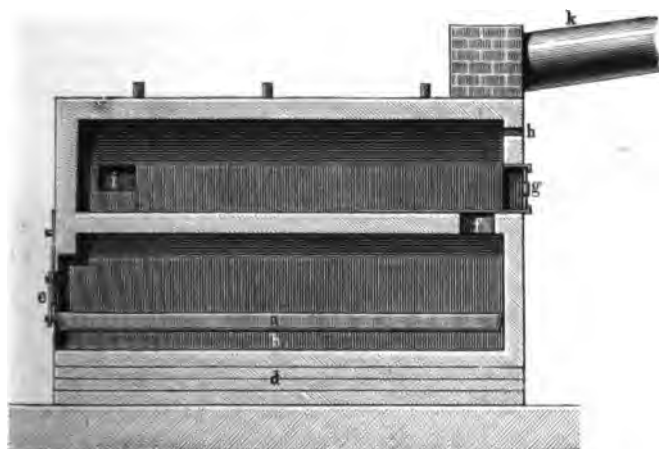
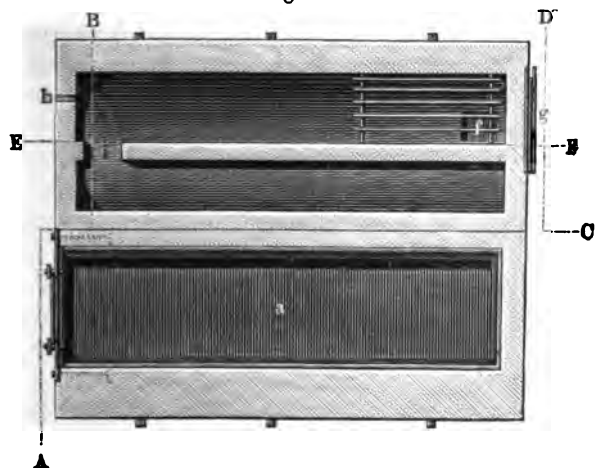


Fig. 25.



to two burners, whose upper stories are accordingly not built identically, but symmetrically.

This burner (known to myself from actual use) admits of very good regulation; the sublimed sulphur on its long way through the upper story is either deposited as such or burnt, and cannot get into the chambers. The boiling-over of the nitre-pots can here be made harmless by simple contrivances. This burner is in some points analogous to that of Harrison Blair (see p. 199), but it is much simpler and adapted for a smaller scale of work. As a rule the working doors are closed within a very small fraction, and the admission of air to the upper story is regulated by more or less closing the hole *b*. Four such furnaces work together; every half-hour one of them is charged with $\frac{1}{2}$ cwt. of brimstone.

In order to avoid the drawback common to all sulphur-burners, viz. the high temperature causing a sublimation of sulphur (which some have tried to avoid by wetting the brimstone with water), and in order even to turn it to use, the cover of the sulphur-burner is sometimes employed for drying wet materials; sometimes it has been made in the shape of a pan for heating water or for concentrating acid, which is the most rational plan.

A large brimstone-burner, covered in with evaporating-pans, is shown in figs. 26 to 28. Fig. 26 is a sectional elevation, on the lines E F G H of fig. 27; fig. 27 is a plan on lines A B C D of fig. 26; fig. 28 a front view. These diagrams, representing a furnace at work in America, have been kindly supplied by Dr. Karl F. Stahl, of Johnstown (Pa.). Its bottom, roof, and sides are formed of cast-iron plates, 1 in. thick, with 6-in. flanges bolted together and caulked with rust-cement. A brick wall, 9 in. thick, is carried all round, leaving a hollow space of 2 in. from the plates; a few of the bricks near the top and bottom are put in loosely, which permits of air-cooling in very hot weather. The lead pans placed on the iron roof are 3' 6" \times 10' 10" \times 7", the weight of the lead being 8 to 12 lb. per super foot. The furnace bottom consists of five plates, as seen in fig. 27; on each of the three front bottom plates (3' 6" \times 12') from 1000 to 1300 lb. of brimstone can be burnt in 27 hours.

An arrangement, made by Kuhlmann, for combining a steam-boiler with a sulphur-burner (1st edition of this work, pp. 139, 140), did not answer at all, and has been given up.

All the sulphur-burners hitherto described are built on the intermittent plan; and unless a number of them were working

Fig. 26.

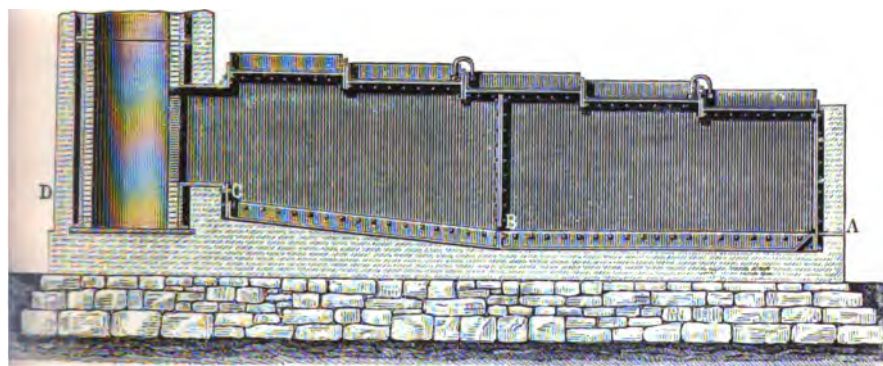
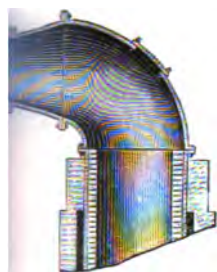
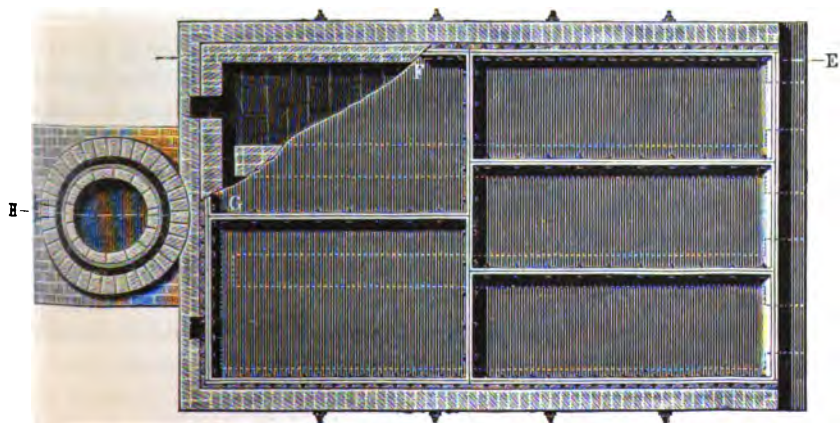
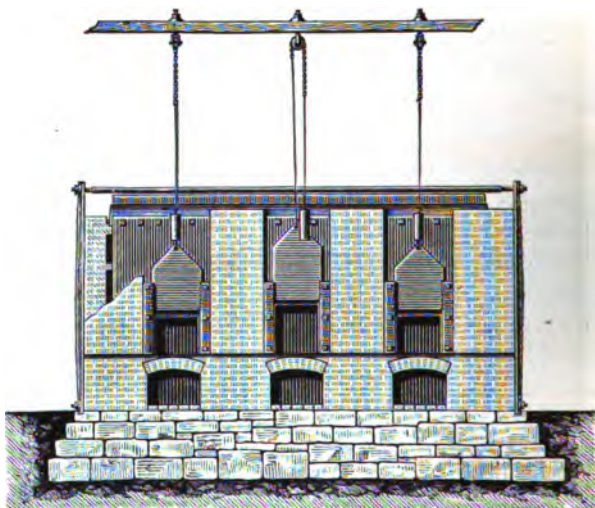
Scale $\frac{1}{72}$.

Fig. 27.



together, they would yield a very unequal current of gas. As the brimstone, of course, must be allowed to burn off as completely as possible, the furnace in the latter stage, and especially just before being recharged, yields very little sulphurous acid, whilst it is not possible to regulate the draught so that exactly so much less

Fig. 28.



air is introduced as less sulphur is burnt. When at last the door is opened for a new charge, a very large amount of air rushes into the burner and further on to the chambers, without any sulphurous acid whatsoever. This irregularity, very prejudicial to the chamber process, is certainly to a great extent neutralized by the fact that always several furnaces (three, four, five, or more) work together in such a way that they are charged by turns; for instance, with a four hours' shift and four furnaces one furnace is charged each hour, and thus gives out least gas when its neighbours are fully burning. It has, however, been several times attempted to construct really *continuous burners*, which would save much labour, and, moreover, give a much better-regulated current of gas than can be given with single burners.

Two such continuous burners have been constructed by Petrie, we refer for diagrams and descriptions to our 1st edition, pp. 141 and 142.

The object pursued by Petrie is attained in a more perfect way

by the furnace of *Harrison Blair*, in which the volatilization of the sulphur, which otherwise is a source of inconvenience, is made use of for making the burning continuous. The apparatus consists of three parts, one of which serves for partly burning the sulphur and entirely volatilizing the unburnt portion; the second serves for completely burning the latter portion, the third for decomposing the nitre. Although both the former compartments are

Fig. 29.

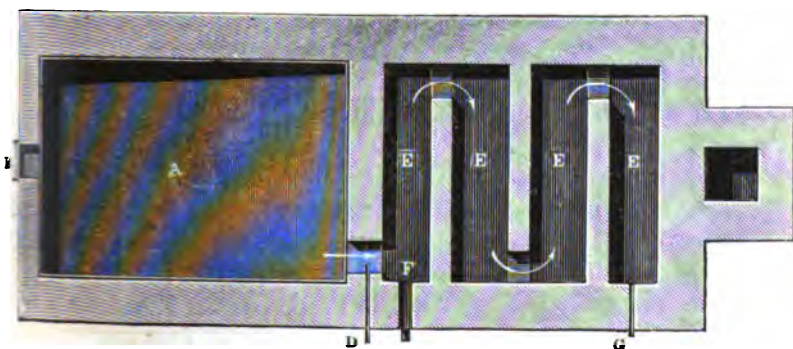
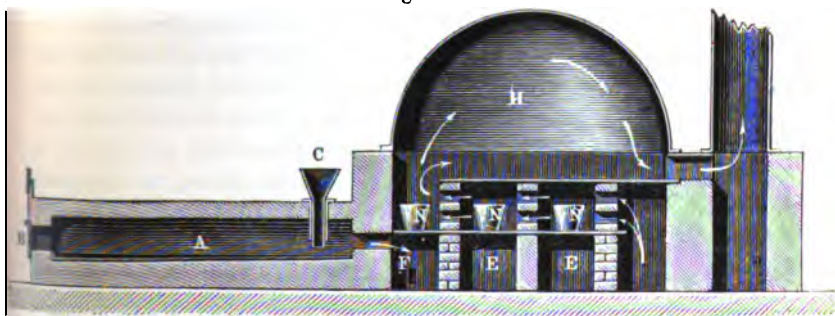


Fig. 30.



at a full red heat during the process, sublimation of sulphur is as good as impossible; and the process is as nearly continuous as possible, since the residue need only be withdrawn once in 24 hours. Fig. 29 shows a plan, fig. 30 a sectional elevation, of this burner. A is the space corresponding to an ordinary burner-plate, which has rather high sides and a descent towards the door; but 2 feet from the door it rises again a little, so that the residue raked to that part can burn out completely before it is removed

by the door B, which takes place once in 24 hours. When this has been done, the residue raked together from the other parts of the burner is brought to the same place and allowed to burn for 24 hours again. The bottom of the burner is not made of iron, but of closely-set bricks with well-grouted joints. This space A is 9 feet long, 6 feet wide, and 1 foot high. The door B is an iron plate, loosely sliding in a frame, but a little slanting so that it closes almost air-tight, and is easily removed. It is perforated by a number of holes, which can be either partly or entirely closed by a slide. The brimstone is either put in once for 24 hours through the working-door, or gradually through a funnel C; C is continued by a 7-inch cast-iron pipe to within 6 inches from the bottom of the chamber; it is surrounded by a wider pipe to protect it against being burnt too quickly. The funnel and its continuation are always filled with brimstone; and this is always replaced again as it melts off at the bottom. The simpler kind of charging once every 24 hours through the door seems after all to have succeeded better. The admission of air through B is regulated so that only sufficient sulphur is burnt for keeping up the heat of the furnace; the largest part is simply evaporated. At the same time the regulation of the access of air allows of spreading the process evenly over the whole day. The walls of the furnace are made $1\frac{1}{2}$ brick thick, in order to keep the heat together. The mixed gas and vapour enters through an opening of 9×9 inches (which can be closed by a fire-clay damper D) into the combustion-space proper, E E, 8×6 feet, divided by three partitions into four compartments, communicating alternately in front and back by openings 9 inches square. Here at the same time fresh air enters by the opening F, which is provided with a damper of 3×8 inches. Now sufficient air is admitted for burning all the sulphur, which can be recognized with certainty by the fact that on opening the plug G the entering air does not produce a new flame. The roof of the combustion-space, E, is formed by fire-tiles, above which a second story, the nitre-oven, is situated. There are three rows of nitre-pots, N, separated by reticulated brickwork, which also serves to support another roof of fire-tiles for covering the nitre-oven, altogether 18 inches high. The diagram shows how the hot gas must circulate round the nitre-pots. The pots are renewed every six hours, so that every two hours another row of pots has its turn. The hot gas, mixed with the nitre-gas, first passes underneath the cast-iron dome, H, for a

partial cooling, then through an iron pipe, I, 24 feet high, into a small cooling-chamber of 18 feet length, 5 feet width, and $1\frac{1}{2}$ foot height (whose bottom and top are covered with water), and then into the lead-chambers. Sometimes steam has been admitted into the combustion-furnace, which is said to hasten the formation of sulphuric acid. With a furnace of the dimensions stated, 26 tons of brimstone per week are said to have been burnt in a perfectly satisfactory way, corresponding to the work of 15 ordinary burners; by cutting off part of the air it was possible to reduce the sulphur burnt to 5 or 6 tons per week. For an equal chamber-space much more sulphur can be burnt than with ordinary burners without any damage to the process, owing to the even work and the avoiding of any excess of air. Indeed Blair's burner is much commended, and probably would have been employed much more largely, but that soon after its invention most large works (and only such can do with it) have passed over from brimstone to pyrites.

Now-a-days, of course, nobody would think of such a way of cooling the gas as is shown here in the cast-iron dome H. We would employ its heat in a Glover tower, or previously for concentrating acid. We would also now-a-days replace the potting arrangement shown in the diagram by the more perfect arrangements to be described further on in connection with pyrites kilns; or we would leave it out altogether, and supply the chambers with liquid nitric acid through the Glover tower.

A modification of the principle of burning the subliming sulphur by introducing air behind the burner has been patented by H. Glover (No. 3774, 1879). He arranges behind the burner a chamber, loosely packed with bricks, in which the vaporized sulphur deposits before it can get into the lead-chambers. This brick chamber, when it is partially filled with sublimed sulphur, is burned out by admitting air into it. The heat is utilized for concentrating acid, and the gases are ultimately passed into a Glover tower, where they do all the necessary denitrating work. This system is at work at a Philadelphia factory, and gives full satisfaction, as observed by myself, no repairs having been required after the lapse of five years.

This arrangement is shown in fig. 30 *a*. A is the usual burner-plate, B the feeding-apparatus (on the same principle as used in Blair's burner); the burner-gases, with the subliming sulphur, pass into the chamber C, where they meet air entering through the pipes F, either cold or previously heated by waste heat. The

mixture further passes through chamber D, containing a network of fire-bricks like that used in a Siemens' recuperator; the mixture and combustion here become perfect, and the gases, now entirely deprived of free sulphur, pass away through H and the flue IK. On their way a platinum dish, E, for concentrating sulphuric acid, is placed on the top of chamber D, and further (lead) pans, J and G, are employed for a first heating of the acid. From here the acid gas passes into a Glover tower, where it is still hot enough to concentrate all the Gay-Lussac acid (equal to $1\frac{1}{2}$ times the daily make of the chambers) up to 150° Tw., and impart to it a temperature of 127° to 132° C. The lead pans G J and platinum dish E produce daily 9000 lb. of acid of 91 or 92 per cent. H_2SO_4 from chamber acid of about 123° Tw.; that is, two thirds of the acid made from the 4000 lb. of brimstone burnt on plate A. Since this acid is taken directly from the chambers (the Glover-tower acid being used exclusively in the Gay-Lussac tower), and since the concentration is not driven to a higher point than 92 per cent., the platinum dish never requires any cleaning out of iron salts &c.

Another sulphur-burner, on the principle of continuously supplying liquid sulphur, is that employed at the works of M. de Hemptinne, at Brussels, and shown in figs. 31 and 32 (taken from the Bulletin du Musée de l'Industrie de Belgique, January 1882, sent to me by the Author). It consists of a cast-iron arch A, strengthened by bracings, and resting on a large flanged wrought-iron plate with flat rivets which can be heated or cooled by flues underneath. On this plate there are placed, side by side and as level as possible, four cast-iron plates with 3-inch upright flanges, intended for burning the sulphur, which is supplied by four spouts from a cast-iron box C, divided in four compartments and built into the front wall, as shown in the diagram. Perpendicular partitions D serve as lutes for preventing the burner-gas from blowing out in front; if the combustion should spread to the front, a cover (not shown here) would at once put the flame out. Thus the supply of sulphur takes place regularly; the four hinged doors *a a* in front serve merely for the entrance of the air and for clearing out the cinders. The arch A consists of ten pieces bolted together; it is covered by light sheet-iron shutters, E E, bent to the same shape and covered with a mixture of loam and straw, which can be raised or lowered by a chain, pulleys, and counterpoises. This admits of regulating the heat of the

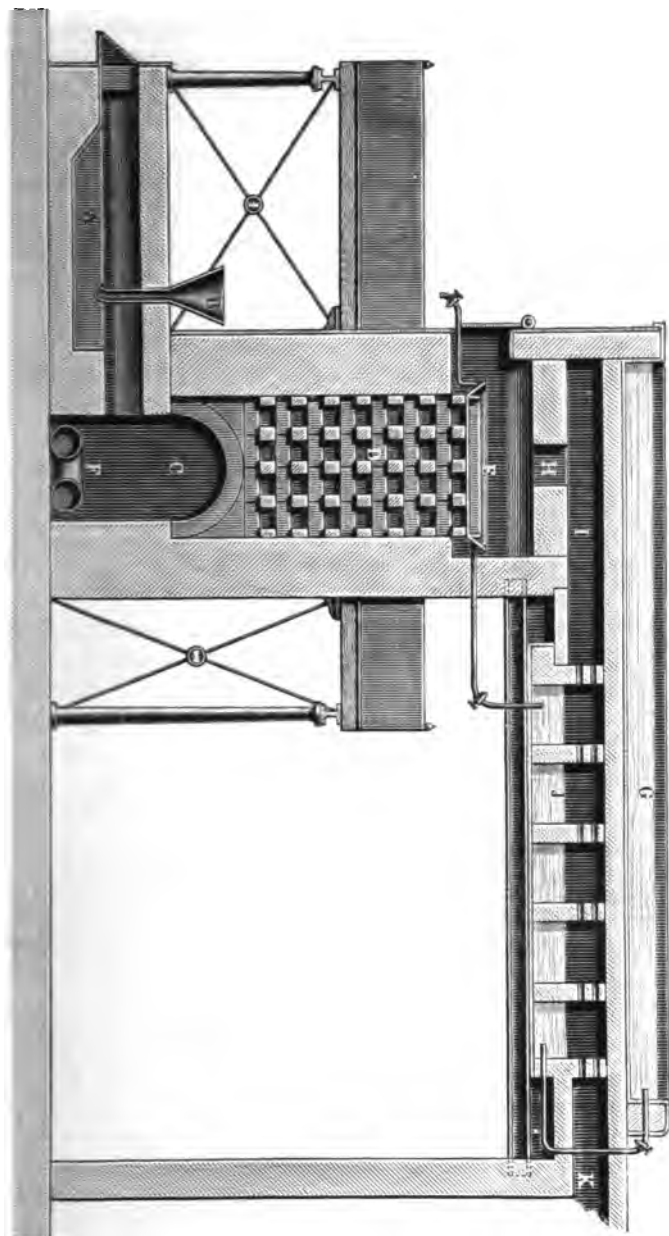


Fig. 30 a.

Fig. 32.

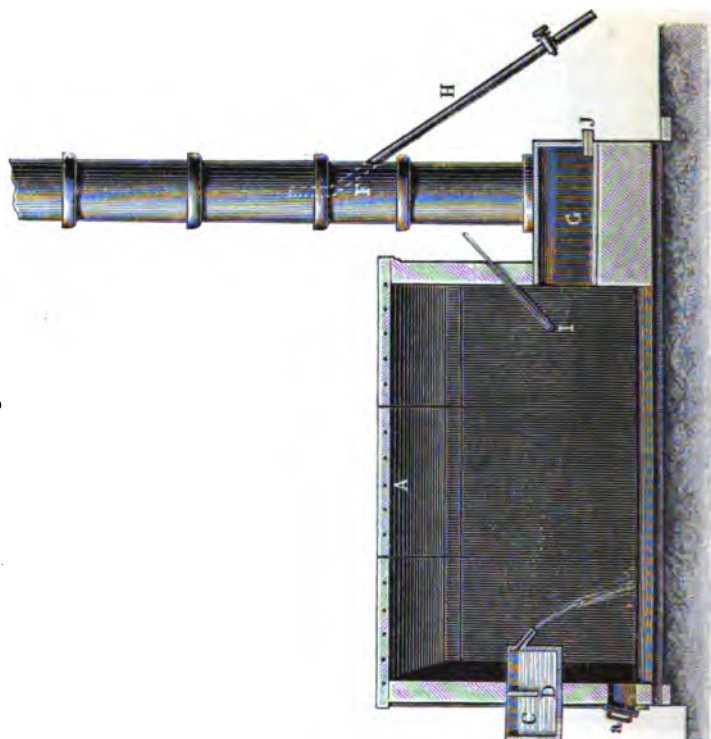


Fig. 31.



chamber; if it rises too much, one or more of the shutters E E are raised. An alarum thermometer, I, in a copper tube, indicates the temperature. The gases escape through the metal pipe F, resting on a thick-walled cast-iron box G, from which the deposit formed can be withdrawn through J. Through H an extra supply of air can be let into the tube F. [This arrangement for supplementary combustion is decidedly imperfect.]

For producing cold and dry sulphur dioxide, free from sulphuric acid, such as is specially useful for preparing liquors for manufacturing wood-pulp, Némethy (G. P. No. 48285) recommends the combination of a sulphur-burner, cooled from the outside by water running down the sides, with a chamber, placed underneath, filled with iron borings, in which the sulphuric acid is retained. From here the gas passes through a number of flat, perpendicular, iron boxes, cooled by water running down their sides, and then into the apparatus, where it is to be absorbed by milk of lime, &c.

W. Maynard (patented as a communication to A. M. Clark, No. 6982, 1884) draws the gas, generated by burning sulphur in cups contained in a chamber, out of the latter by a goose-neck pipe leading from the top of the chamber to a closed box provided with a funnel delivering into another box below. Water is delivered by a pipe into this funnel, which has grooved sides, so that the liquor running round as well as downwards forms a vortex, and draws away the vapours generated in the burning-chamber. This arrangement is evidently not intended for sulphuric-acid making, but for preparing a solution of sulphurous acid.

The following arrangement, by Körting Brothers, serves for preparing comparatively small quantities of sulphur dioxide from sulphur, for bleaching, in the manufacture of glue, for saturating the liquors in sugar-works, and the like. A (figs. 33 and 34) is a cast-iron retort provided with a perforated dish *a*, in which the sulphur is placed. B is a Körting's injector, made of hard lead (5 lead, 1 antimony), which, by means of a steam-jet, aspirates air through the holes *b b* into A and causes the sulphur to burn. The vapours are forced downwards in the inner tube of the cast-iron cooler C, whilst cold water flows in the annular space between the two tubes, entering at the bottom and running out at the top. The box D, on which the cooler is mounted, serves for retaining any sublimed sulphur and other impurities. From here a tube leads the purified SO₂ to the place where it is to be utilized.

Fig. 33.

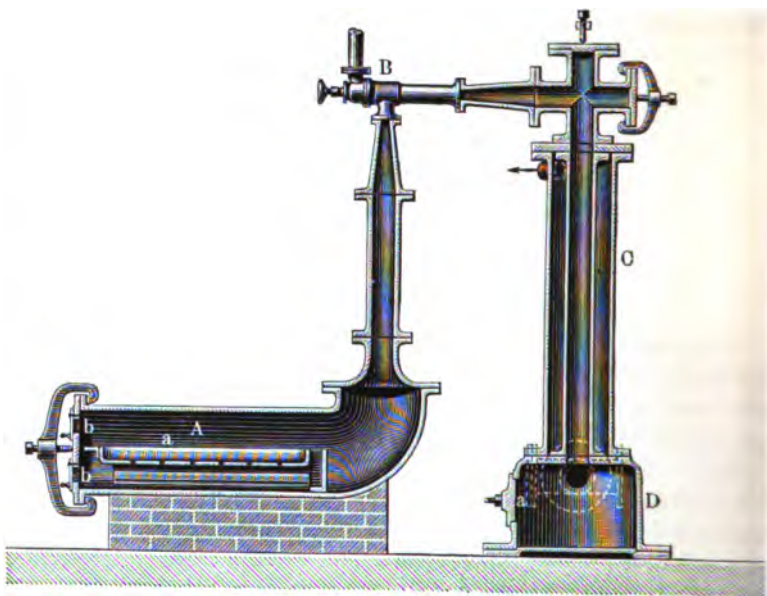
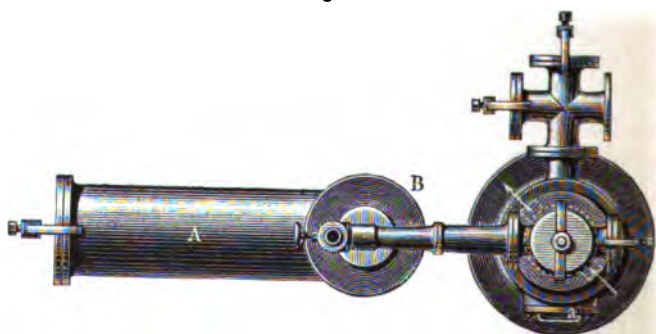


Fig. 34.



The following analysis of the residue from the sulphur-burners has been made by Richardson (Richardson and Watts, 'Chemical Technology,' vol. i. pt. v. p. 198) :—

Sodium sulphate*	13·77
Calcium sulphate†	28·49
Calcium silicate†	15·91
Sodium silicate	1·10
Ferric oxide and alumina	2·80
Water and sulphuric acid*	13·05
Insoluble	24·29
	<hr/>
	99·41

A special *cooling of the gas* from sulphur-burners is, as a rule, not only unnecessary, but even injurious ; so that, for instance, in the furnace shown in fig. 22 the vertical metal pipe conveying the gas to the chamber had to be protected against cooling by a brick jacket. Even where no cooling takes place by water-pans, steam-boilers, &c., the gas gets into the draught-pipe sometimes at only about 100° or 120° C. temperature, which is just sufficient not to allow the nitric acid to condense before it gets into the chambers, a contingency decidedly to be avoided. Where water-tanks, acid-pans, &c., are used, the temperature of the gas is said to come down as low as 40° C. ; in this case only liquid nitric acid can be used for the chambers. In Blair's or Glover's continuous burner the temperature certainly rises much higher ; and in this case a cooling-arrangement, such as that described, was formerly thought indispensable, before means had been found of utilizing the heat of the gases in a Glover tower or otherwise.

B. THE PRODUCTION OF SULPHUROUS ACID FROM PYRITES.

1. BREAKING THE PYRITES.

The pyrites, as it comes into the market, is always sufficiently pure to make a separation from gangue unnecessary, except in the case of pyrites picked from coals ("coal brasses") ; but this is only a locally-used by-product.

* The sodium sulphate and the free sulphuric acid (or rather the acid sulphate) evidently come from the nitre-pots boiling over.

† The lime no doubt partly comes from the brickwork of the furnace.

It is, however, always necessary to break up the larger lumps in order to burn the pyrites completely; and this is always done at the works themselves—except in a few cases, where they buy smalls direct from the mines. The majority of the factories break the ore by hand; and it is found that different descriptions of ore behave very differently in that respect. The Norwegian ore is the hardest; here the large lumps have to be broken with great labour by means of 20-lb. fore-hammers. The Westphalian ore is much more easily broken—still more easily the Spanish and Portuguese and some of the French ores; these, however, make a good deal more smalls, 10 per cent. and more. The softest ore is that of Chessy, consisting of loosely aggregated individual crystals, which by a blow of the hammer fall to powder. Some of the Spanish ores are equally roughly crystallized; these ores are very troublesome for use as lumps.

In England the ore is generally broken so that all the pieces pass through a sieve with 3-inch holes. At Oker only pieces of $1\frac{1}{4}$ inch side are allowed for ordinary burners, and of $2\frac{1}{2}$ inches for deep kilns. On the other hand, as few smalls as possible are made. The broken ore must be sifted again to separate the smalls, for which purpose some works pass it through a half-inch, others through a quarter-inch riddle. What remains on the riddle is *lumps*; what passes through, *smalls* or *dust*. Both of them have to be treated separately. It is very important that the ore be used neither in too large nor in too small pieces. In the former case it does not burn right through; there remain green cores in the interior of the cinders, which can be seen on breaking them up. These large lumps also get too hot on burning, and may cause the formation of slags (scars) by production of FeS , as will be explained hereafter. If, on the other hand, the pieces are too small, they too much prevent the access of air, and similar results follow from it as in the former case.

It is quite obvious that the pyrites-burners can be worked to full advantage only if the ore is in pieces of as uniform size as possible, and it would hence be the best plan, although it is hardly practicable in reality, to separate the broken ore into a number of sizes, to be burnt in separate kilns. This is best proved by the following argument, taken from Dr. Hurter's lecture on the Manufacture of Sulphuric Acid (Liverpool, 1882, p. 5). Upon a regular continuous flow of sulphurous acid depends the success of

the other operations. When a chemical action, such as combustion, takes place, the rate at which that reaction proceeds depends in the first instance upon the surface of contact between fuel and air; in the second, upon the velocity of the air. The surface of contact is, of course, the sum of the surfaces of the single pieces which form the layer upon the grate. For a certain velocity of air there is required a certain amount of surface in order to yield a particular composition of the products of combustion. For a certain depth of the layer a certain velocity of air is required, but just as much a certain size of the pieces, as upon this depends the surface of contact; and if the latter is varied, either the depth of the layer or the velocity of the air, or both, must be varied in proportion, if the proper composition of the gas is to be attained.

Owing to the great manual labour required for the breaking of pyrites, the same *mechanical stone-breakers* have been introduced for this purpose which originally were made for road-metal. The best of these machines is that of Blake, built by Messrs. Marsden of Leeds, which is shown in figs. 35 and 36. This machine is made of various sizes, and accordingly varies in the amount of work turned out and in the size of stones it can attack. A and B are the two active parts, the "jaws." A is fast and perpendicular, B movable, and makes with A an angle of 72° , by oscillating a little round the fixed shaft D. This movement is communicated to the jaw B from the main shaft, H, by means of the angle-lever, E E', and the crank motion, G H, so that the angle-lever presses the jaw B against the stones charged, the return motion of B being caused by a spring, F, cased in india-rubber. The angle-lever is adjustable by the wedge, N, lying behind its arm E'. The roller, C, causes a regular throwing-out of the broken stones; it receives its motion by a belt from the main shaft, by means of the pulleys, K, L, and the expanding roller, M. The crank-shaft, H, is also driven by a belt from the fast and loose pulleys, I I'. The machine is mounted on a four-wheeled bogie. It makes a great deal of noise and needs frequent repairs; but the jaws, which principally suffer, are so arranged as to be easily replaced.

Blake's engine has been improved by Broadbent & Son, of Staleybridge, who have replaced the spring bedded in india-rubber by a simple, easily-adjustable lever arrangement, which saves labour as compared with the original arrangement. Output, according to size, from 40 to 130 tons in ten hours; price £140 to £375.

At Oker, a steam-engine of 12 horse-power drives two stone-breakers, mounted one above the other. The higher one breaks

Fig. 35.

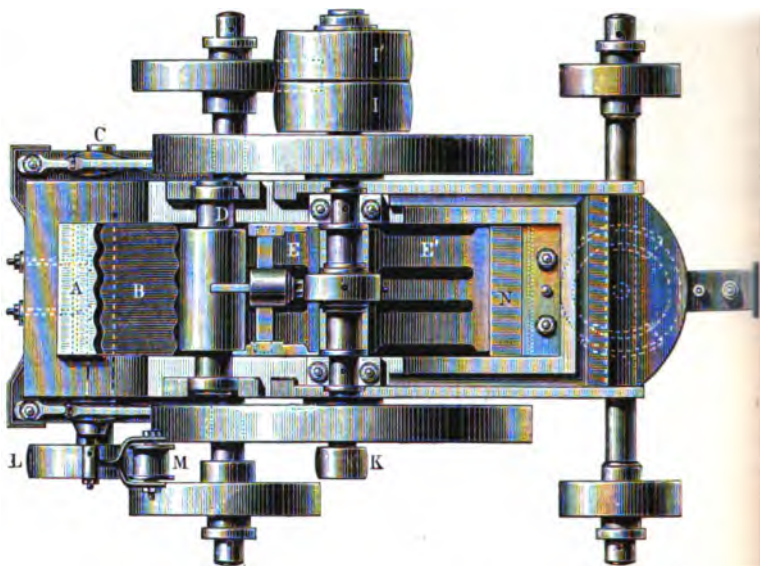
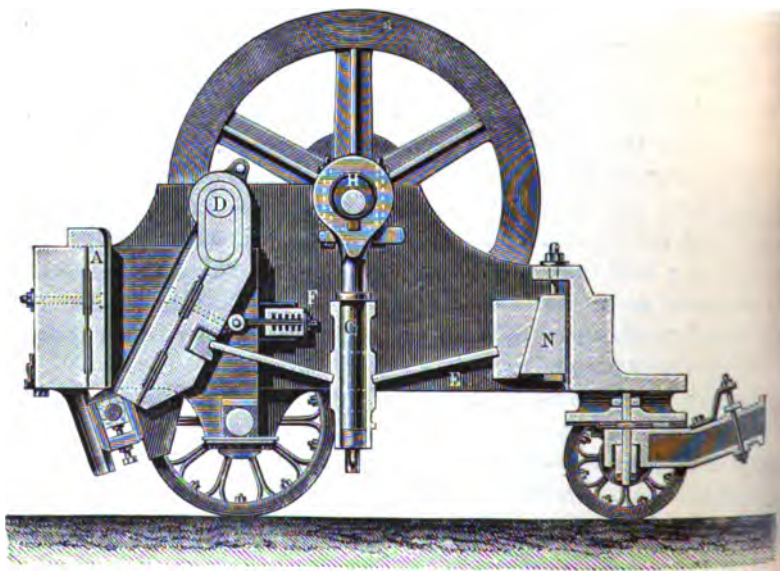


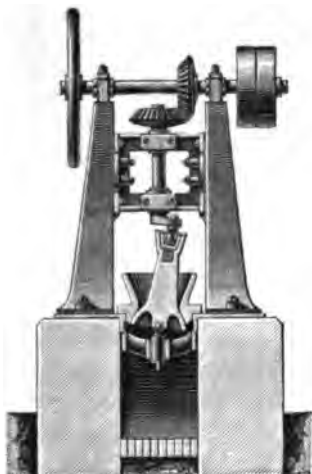
Fig. 36.



the large stones roughly, the lower one down to the proper size. They supply, in the case of very hard ore, and a size of $1\frac{1}{4}$ inch, 25 tons daily ; at $2\frac{1}{4}$ inches size, 40 tons.

A crushing-mill was invented by Motte, at Dampreny, near Charleroi, which has been improved by the Markish Engine Works (German Patent, October 16th, 1877 ; 'Dingler's Journal,' ccxxvii. p. 58). The principle is that of a peculiar kind of mortar, with hollow bottom, in which the crushing is done by a pestle, as seen in fig. 37. Whether this mill is really preferable to the older stone-breaking machines experience will show.

Fig. 37.



Durand and Chaptal's stone-breaker consists of a number of hammers attached to a horizontal revolving shaft. It is said to make less dust than other stone-breakers. The smallest apparatus breaks from 8 to 25 tons of stone in 10 hours, with an expenditure of 2 or 3 horse-powers, the larger size from 80 to 130 tons, with 6 horse-powers.

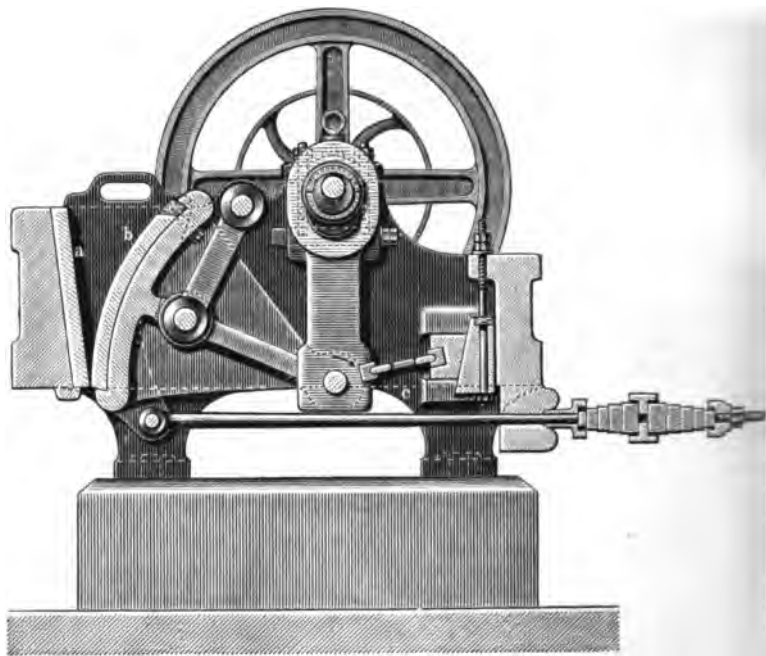
Vapart's breaking-mill (address, "Chênée, Vieille Montagne") works with centrifugal force.

The Humboldt Engineering Company at Cologne (Germ. Pat. 1906, Jan. 12, 1878) manufacture stone-breakers which do twice the work of those formerly in use, with the expenditure of the same force.

Other improvements in stone-breakers have been invented by Brown (*Scientific American*, 1879, p. 194) and Welter (German patent, No. 7494, March 5, 1879).

A machine very much recommended is Breuer's "Sectorator" (G. P. 30477), supplied by Ernst Maetz, Berlin, S.W. As shown in fig. 38, it contains a straight breaking-jaw, *a*, firmly connected

Fig. 38.



with the solid frame, whilst the movable jaw, *b*, is suspended in two steel trunnions, and is partially revolved against the jaw *a*, thus crushing the material. The angle between the two jaws is rather acute, so that large pieces are easily caught and carried forwards towards the bottom slit. If both jaws were arched, the material, especially large pieces, would be able to escape upwards for a long time, until gradually broken up. The width of the bottom slit is adjustable by a wedge even during work, so that any size can be obtained. The plate *c* behind the excentric sheave, which is easily exchanged, is of cast-iron and of a smaller section

than any other part of the machine subjected to a breaking-strain, so that in case of excessive strain by the passage of a foreign body (iron, &c.), that plate must give way before any other part of the machine.

Even at some large works they prefer dispensing with mechanical stone-breakers, principally for two reasons. The first of these is that they make more dust than breaking by hand; but since dust is now even more profitably burnt than pieces, this reason is no longer valid. The other reason is, that at large works there is always a certain number of men who are incapacitated for other work, or who are temporarily unoccupied, and these are best set to stone-breaking.

2. PYRITES-BURNERS FOR LUMPS.

Among the apparatus for burning pyrites in the manufacture of sulphuric acid, a distinction has to be made between those intended for lumps and those intended for smalls. It is indispensable to keep both kinds apart, and to employ different apparatus, or at least processes, for them; for if the broken ore is put into the burner without separating the smalls, the air-channels, which ought to remain between the pieces, are soon partly stopped up with powder, and the access of air becomes irregular; thus scars are formed, and proper work is then impossible. Apart from the coarser and finer powder obtained on breaking, a great deal of smalls comes into the trade direct from the mines, obtained there by the use of water for separating the ore from the gangue.

Where cupreous pyrites is roasted without any regard to the utilization of the sulphur, the only object being the extraction of the copper, usually no regular kilns are employed at all, but the ore is burnt in "heaps." This is done on an enormous scale in the south of Spain; but the damage done to health and vegetation has been so great that a law has been made compelling manufacturers to abate this nuisance. In order to avoid the necessity of building the very large number of closed kilns which would be required for that operation, various proposals have been made. We quote that of Fleming (E. P. 10153, 1887). Above the roasting-heap, and extending downward over the whole portion (about one-third) which emits the fumes, is suspended an iron hood, lined with tar and painted outside with a non-conducting

material. The hood is supported by chains from two pairs of shear-legs, and the whole is strengthened by iron stays. At one end of the hood is a pipe, by which the roaster gases are led to condensing-flues, to separate arsenious acid, and thence into vitriol-chambers. If the gases have excess of air, they are led through calcining-furnaces; if insufficient, more can be supplied by regulating-dampers in the flues. [Apart from all other objections to this process, the "iron hood lined with tar" is sure to be a very short-lived affair.]

The burning of pyrites in lumps (pieces) for the manufacture of sulphuric acid is always done in such a way that the combustion heat of the pyrites is utilized for maintaining the process without employing any extraneous fuel. The apparatus used for this purpose are called "kilns" or "burners." In the first edition of this work (p. 151 to p. 154) there will be found a description of the old and now abandoned kinds of kilns, with many diagrams, as the burner originally employed by Farmer, the first shape of tall kilns without grates, the Oker kilns for roasting the Rammelsberg ores. These kilns (except Farmer's) are constructed without grates; they are still used for roasting poor ores, lead-matt, &c., but not for the proper manufacture of sulphuric acid, for which the burners ought always to be constructed with grates and ash-pits. This causes a considerable improvement in the working of the furnaces. Where the air has merely to pass through a mass of burnt ore, its quantity cannot possibly be regulated at the inlet, but only by dampers at the other end of the furnace. It is even a more serious disadvantage that the subdivision of the air inside the burner must be very irregular in that case. According to the greater or smaller resistance offered by the individual portions of the layer of pyrites, the air will pass through very unequally, and in less quantity at the places where most pyrites is lying and where it is most wanted. The addition of a grate and a closed ash-pit alters the state of the case at once, in this way, that only a definite quantity of air need be admitted into the ash-pit, and that, moreover, this air must first spread equally underneath the grate and rise all over the area of the burner. Thus the ore is much more completely burnt, and at the same time richer gas is obtained, which leads to a better chamber-process, higher yield of acid, and smaller consumption of nitre; the operation of drawing out the burnt ore becomes much more regular and offers a greater guarantee

against raw ore getting into it; lastly, it does not happen so often that fused masses, "scars," are formed in the burner, although also in the case of grates this easily happens if the style of working is faulty.

The introduction of grates led to further improvements:—first, a diminution of the height of the burners, which made them much handier for working, and which acted especially well with more easily fusible ores, although in some places the other extreme of

Fig. 39.

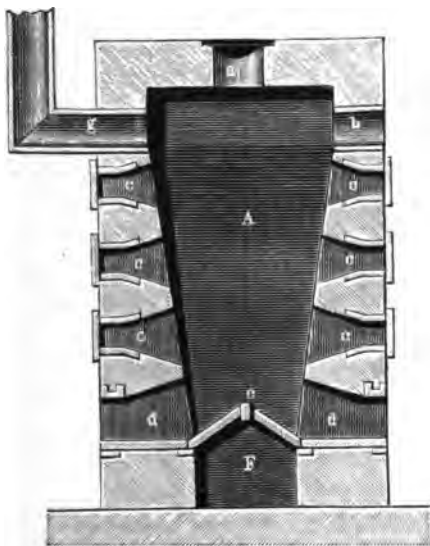


Fig. 40.



too low layers of pyrites has been resorted to. Also the way of introducing the nitre has been very much improved; but in many cases this has been a sore point, even up to recent times. The mixture of nitre and sulphuric acid is very apt to boil over; and the running-over acid saltcake, if it gets into the burner, is not merely lost, but it disturbs the draught, and causes the ore to cake together in extremely hard masses, which can only be removed after pulling down the front wall. Other improvements will be mentioned later on.

A transition from the metallurgical kilns to the burners of to-day is presented by the Freiberg kilns for roasting 18 or 20 cwt. of coarse metal, with 20 or 21 per cent. of sulphur, in 24 hours (figs. 39 and 40). *A* is the shaft; *a*, charging-holes, 12½ inches wide, covered with iron plates, upon which a layer of coarse metal, 1 or 2 feet deep, is tipped; *b*, three larger working-holes, 15 inches long by 12 inches high; *c*, three rows of working-holes, 8 inches by 4 inches; *d*, three drawing-out holes on each side, 2 feet by 1 foot; *e*, saddle-grates; *F*, air-flue; *g*, flue for taking away the sulphurous acid. The saddle-grate is for the purpose of conveying air into the middle of the shaft, where it penetrates less easily than along the sides.

In our first edition, pp. 157 and 158, there is a description of the Belgian hearth-furnaces and of the Marseilles burners (with diagrams), which we omit here, as both are very faulty and quite antiquated.

We approach the constructions of to-day with the Freiberg burner, shown in figs. 41 to 43. Fig. 41 gives an elevation through *c d* and *d e* of the plan, fig. 42, on a scale of 1 : 50; fig. 43, a sectional elevation through *a b* of the plan. This burner is specially adapted for easily-burning ore. *B* is the shaft; *f* the charging-hole, furnished with a tightly closing cover. The grate, *g*, still shaped like that of a steam-boiler, is inclined, in order to facilitate the drawing through *h*. The smaller pieces fall through the grate into the ash-pit, *A*, and are emptied from time to time through the door, *i*, furnished with holes for the supply of air. About 10 inches above the grate the front wall of the burner is pierced by a horizontal row of holes, *k*, in which stuffing-boxes are fixed for movable round iron bars, *l*. These can be used for loosening the ore (which they will do very incompletely); they also serve for supporting the higher-lying portions of ore on with-

Fig. 41.

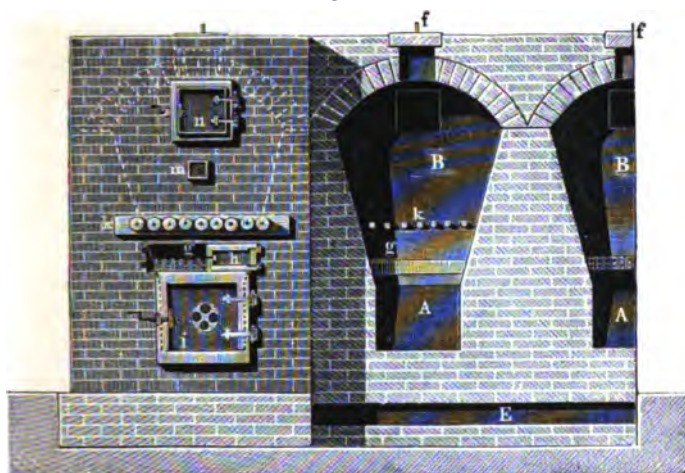
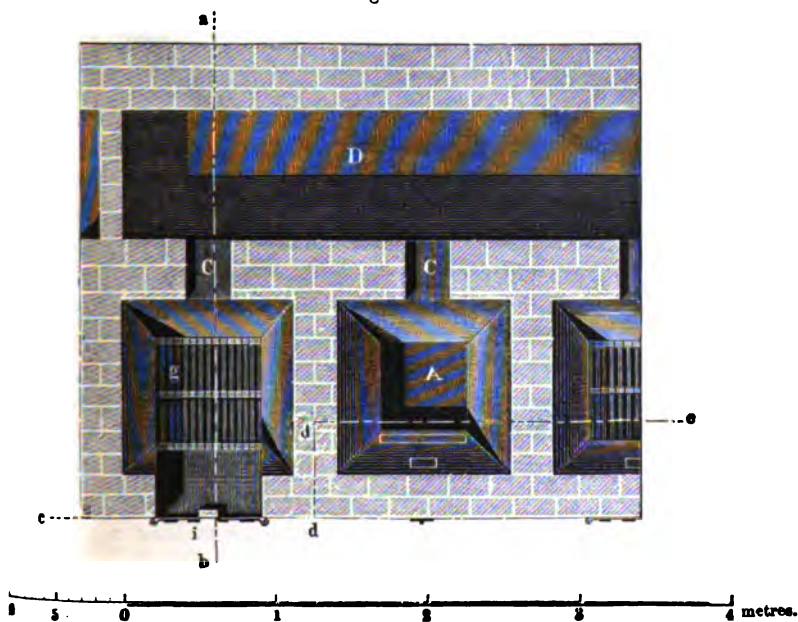
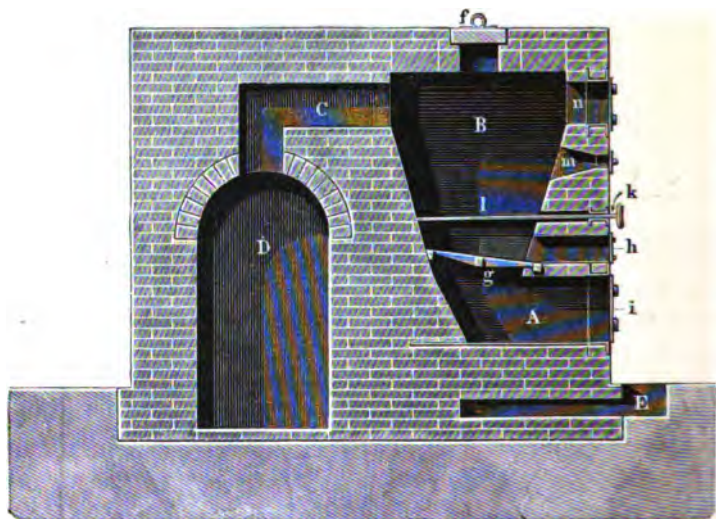


Fig. 42.



drawing the cinders. The door, *m*, serves for observing the combustion (which, however, can only be judged of properly from the top) and for introducing a poker in case the ore must be broken

Fig. 43.



up. The larger opening, *n*, likewise with a door, serves for the same purpose, and also for potting in the flue, *C* (which must be a very troublesome thing, looking at the large size of *B*, connected with great risk of spilling the contents of the nitre-pots). The gases from *C* get first into the large main flue, *D*, which at Freiberg is upwards of 330 feet long; here they deposit dust, and especially arsenic, and then pass on to the acid-chambers. The flue *E* serves for keeping the ground-moisture from the burners.

Whilst on the Continent there was still an oscillation between the extremes of high kilns and of hearth-furnaces, in England already, since about 1860 or 1862, an intermediate form had been found, which, in all essential parts, is the same as that used now, and is being more and more introduced on the Continent. The English pyrites-burners have a moderate area of grate, about 4 to 5 feet wide, and $4\frac{1}{2}$ to 6 feet from front to back. The inner walls sometimes rise quite perpendicularly; more frequently the two sides and the back slant a little outwards, up to the level of the

working-door, to the extent of about 9 inches, sometimes only 6 inches, in width, and half as much in the back; from that level the walls rise again perpendicularly up to the roof. The front wall, which is only 9 inches thick, and mostly protected by a 1-inch or 1½-inch metal plate, rises perpendicularly, and is perforated with several working-holes. The ash-pit has either vertical sides or, more rarely, sides converging towards the bottom, in order to facilitate the removal of the cinders. Its depth varies from 16 to 24 inches. The level of the working-doors, which determines the depth of the layer of pyrites, varies from 1 foot 8 inches to 2 feet 6 inches; but the former depth is considered by most practical men too little, at any rate for average ores, and the right depth is between 2 feet and 2 feet 4 inches, but nearer the upper than the lower limit. At the Oker works the depth of ore is only 1 foot 6½ inches, and elsewhere in Germany similarly, even down to 1 foot 4 inches. The reason of it is the fear of scarring, which English experience with the same ores proves to be unfounded. The height from the upper level of the ore up to the abutment of the arch is usually about equal to that of the working-door, say 9½ to 12 inches, and from there up to the crown of the arch another 8 or 9 inches. The arch itself is either sprung from side to side, as is the custom on the Tyne (whereby the walls are made to bear the weight more equally and the working through the doors is facilitated), or, as is usual in Lancashire, from front to back (which is more advisable in the case of two rows of burners being built back to back, in which case the arch is sprung over both burners together, with a supporting wall in the centre). In any case it is advisable to build the burners back to back, even with arches sprung from side to side, wherever it is locally possible; thus one back wall is saved, the heat is kept up better, and a common gas-flue can be employed.

The *gas-flue* of the English burners is always at the top, each burner-arch having a hole of 4 to 5 inches square leading into it. These holes are not always provided with dampers; but by gradually increasing the size of the hole as the distance from the main shaft becomes greater, evenness of draught is produced. The flue itself can be made of bricks set in tar and sand, and covered with fire-tiles. Most modern works prefer forming it by a second arch, about 6 or 12 inches above the burner-roof, reaching right across the whole burner, and supported by the front plate being made high

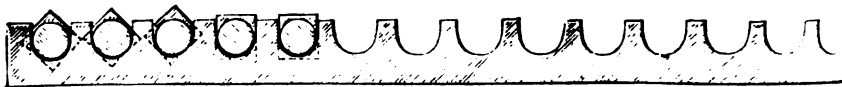
enough. Special care is devoted to the *doors*, as will be seen when we give the detailed description.

The principal feature of the English pyrites-burners, which has now been introduced into nearly all continental works as well, is the employment of grate-bars of square or oblong section, movable in bearings, and leaving larger or smaller spaces between them, according to their position. (According to Hasenclever, in Hofmann's 'Bericht,' 1875, i. p. 158, movable grate-bars have been used in France ever since 1848.) Fig. 44 represents such a grate-bar, in which the places can be noticed which are forged or cast round, so that they can easily turn in the respective hollows of the bearers. Bars 2 inches square are usually made of wrought iron; the oblong bars, 2 by 3 inches, which, being turned on edge, leave a

Fig. 44.



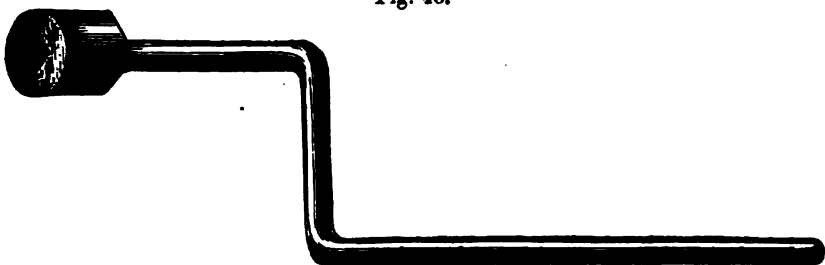
Fig. 45.



larger space, and therefore only suit larger pieces, are mostly of cast iron. The grate-bars rest on cast-iron bearers, as shown in fig. 45; in the shallower kilns ($4\frac{1}{2}$ to 5 feet from front to back) there are two such, in the deeper kilns (5 feet 3 inches to 6 feet from front to back inside) three. According to this, of course, two or three rounded places must be made on the bars themselves. Lest these should be weakened too much, the diameter of the round places in the square bars is equal to the side of the square, in the oblong ones equal to the smaller side. In any case the front piece of each bar, where it projects beyond the bearing-bar, remains square or oblong, so that it can be turned round its axis by means of a suitable key (fig. 46). The intervals between the grate-bars are mostly managed so that with 2-inch bars they are about 2 inches when the bars are in the situation shown in fig. 47; but if they are turned 90 degrees, as in fig. 48, the intervals will only amount to $1\frac{1}{4}$ inch. In another actual instance the diameter of the bars

was $1\frac{1}{4}$ inch, the clear distance in the straight position $1\frac{1}{4}$ inch, in the diagonal position 1 inch. If, lastly, the situation is as in fig. 49, where half of the bars are turned, the intervals will be between the

Fig. 46.



two above limits; and as each bar can be turned separately, many combinations can be produced. Usually the bars stand as in fig. 48—that is, all with their diagonals in a horizontal plane, or with the smallest possible intervals, so that the pieces of ore cannot fall through. As soon as a portion of the ore has to be removed, the attendant takes hold of the front end of the bar with

Fig. 47.

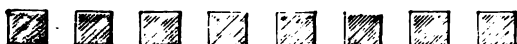


Fig. 48.



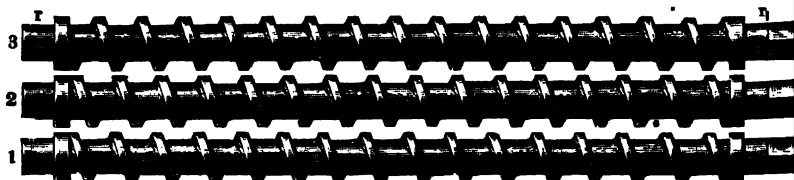
Fig. 49.



his key, and moves it a few times from side to side. Thus a kind of crushing action will be exercised on the cinders getting between the two bars, the intervals are momentarily enlarged, and that which is jammed between the bars is forced downwards. Of course a good deal of strength is required for this work. At the same time, by the action of the key, the pyrites is loosened up to a certain height. The workman now goes from one bar to another, generally leaving one out, and shakes them according to the judg-

ment of the eye, so far that an equal quantity of burnt ore is drawn out all over the area of the grate. That which has fallen through is allowed to lie in the ash-pit till the time comes, once every 24 hours, for opening the bottom door and taking away the cinders. A new shape of bars, which is said to possess great advantages over the ordinary angular ones, has been patented by W. Helbig (Dingl. Journ. ccxxvii. p. 67) and is shown in fig. 50. It is that of a cast-iron bar, of round, square, or elliptic section, with a worm all round it. The pitch and cross section of the thread are made to suit the maximum and minimum size of the pyrites for which the grate is intended. The collars, r and r' , protect the bar from getting out of its bearings; c is the back bearing, f the front bearing, with a square continuation for receiving the key. The diagram shows the different positions of the bars. When they stand as 1 to 2, they offer the smallest, when they stand as 2 to 3, the

Fig. 50.



largest openings. In either case the total area of the openings is always the same, different from the ordinary burner-grates. Helbig claims the following advantages for his bars (which, however, are partly shared by the usual ones):—The bars, owing to their round shape, are more easily turned, without lifting or shaking up the pyrites; so that no incompletely burnt pyrites comes down too quickly. [This does not seem very advantageous; the shaking up of the ore is even useful in order to prevent it from getting fast.] When larger pieces are jammed between the bars they can be broken up more forcibly. The ore is very evenly burnt, owing to its going down so evenly. On account of the peculiar front bearings, no air can enter there. No pyrites falls out without turning. The injurious effect of the pieces bursting is counteracted [in what way?]. That the grate-surface remains the same in each position of the bars is of vast importance for the regularity of the burning.

These grates are said to be as well adapted as Walter's burners for the burning of "peas" (see below).

It is very acceptable (but rarely met with, because it necessitates a somewhat complicated plant) if the ash-pit is deep enough for introducing an iron bogie below the grate whose top equals the whole surface of the grate in size; the ash-pit door, of course, must be correspondingly large. The cinders in that case fall direct into the bogie, and can be wheeled out in a few moments; usually they have to be raked out by hand, during which time the door must stand open, and much false air gets into the burner. Where there are not two rows of burners built back to back, it is possible to charge on one side and discharge on the other; but there is no great advantage in this arrangement, which takes a great deal of space.

The discharging of the burnt ore is sometimes expedited by iron bogies running on tramways, which are introduced into the ash-pits, and into which the cinders fall as the grates are shaken. This very suitable plan necessitates a system of tramways and turn-tables, as well as a lowering of the whole floor. The following simple and equally efficient plan seems therefore worthy of recommendation. It is a tilting-box (figs. 51 & 52). There are two independent parts:—first, an iron box, of suitable dimensions, with two outside pivots near the upper edge; secondly, a light but strong wheeled frame, which ends in forks fitting under those pivots. As shown in the diagram, the whole is used in the manner of an ordinary iron wheelbarrow on any hard ground. But by lifting up the handle the box is first lowered to the ground, then the forks slip out and the frame can be run back. Similarly the box is taken up again by running the frame in, and depressing the handles till the forks take hold of the pivots. The boxes can be made to fit into the ash-pits, and the cinders discharged into them directly from the grates. Of course other applications of this barrow will present themselves in chemical works.

In the South of France burners are used, 5 feet 11 inches deep, with a grate-surface of 13 square feet, and a distance of $1\frac{1}{2}$ inch between the bars when in a vertical position; in these, lumps, along with 10 or 15 per cent. of "balls," are burnt down to 2 or 3 per cent. of sulphur (Favre, 'Moniteur Scientif.' 1876, p. 270).

In order not to be obliged to open the whole ash-pit when shaking the bars, all better furnaces are provided with a slit in the

front plate, through which the ends of the bars are accessible. Except during shaking-time, the slit is covered by a door, which is best made in two halves.

Norrington (E. P. no. 4131, 1878) makes the ash-pit doors to

Fig. 51.

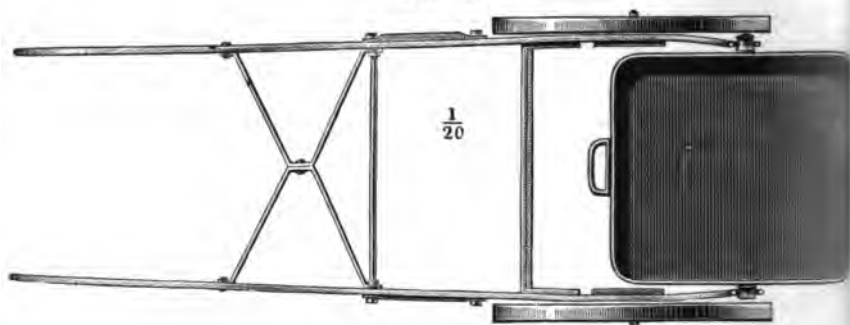
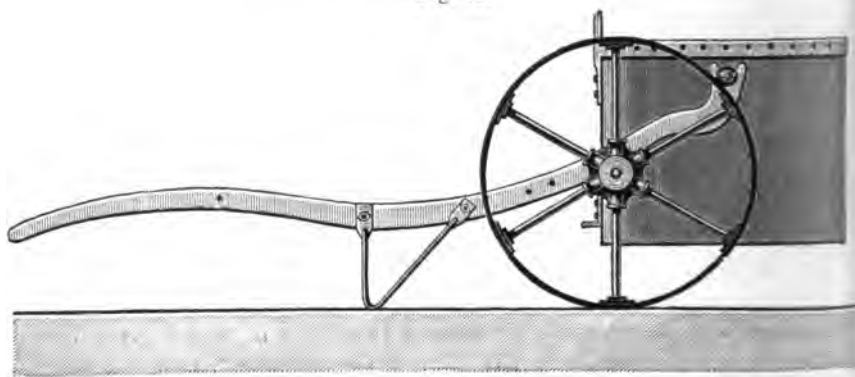


Fig. 52.



slide in horizontal frames, and connects all the doors of a set of burners by jointed rods, so that they can all be moved together in a horizontal plane by means of an endless screw and gearing at one end. All the ash-pit doors are thus opened and shut at the same time. This is always done whenever any one of the working-doors is opened so that no gas can blow out, as the air cannot enter in any other way. According to information from Messrs. Charles Norrington & Co., Plymouth, this arrangement produces a considerable saving of nitrate of soda and of sulphuric acid; owing

to the regularity of draught, all kilns burn equally well. This statement is confirmed by Dr. Ballard (Report to the Local Government Board, 1879, p. 180).

According to a communication from Mr. K. Walter, a simple means of preventing the blowing out of gas at the working-door during charging is this: to arrange a flue underneath the burners, in connection with the chimney, which is opened during the charging just sufficient to prevent any blowing out at the working-door. Less gas is lost and less nuisance is produced in this way than is otherwise the case from the working-doors. With this arrangement the ash-pits require only loosely put-on wrought-iron doors. (In England it would probably not be allowed to draw the gas into the chimney, even for a short time.)

In properly constructed pyrites-kilns, all doors for charging, working, shaking of the bars, and getting out the cinders either run horizontally in grooves, or, still better, they are hung on hinges; and the door-frame, cast upon the front plate, is made to slant forwards below, sometimes also sideways, so that the door lies fast upon it by its own weight. As both the door-frame and the edges of the door touching it are planed, the doors close tight without any luting, whilst those running in grooves must be made tight with lime-putty.

All brickwork, so far as it is touched by the heat (that is, the walls above the grates, the arch, and the gas-flue), is lined with fire-bricks; the total thickness in front is one brick, behind (or as the partition between two rows of burners) two bricks. The side walls dividing each two burners of a row are $1\frac{1}{2}$ or 2 bricks thick, but they diminish upwards to one brick. The roof need only be $\frac{1}{2}$ inches thick. The mortar is fire-clay, as usual; in the colder parts, such as vertical gas-shafts, flues, &c., this does not stand so well as boiled-down tar and sand.

Of course the burners are well bound together, either by special uprights and tension-bars, or by flanges cast to the front plates, provided with holes for the cross bars (fig. 55).

Opinions as to what size the burners are to be made vary a good deal. Mostly smaller burners are met with, about 4 feet 6 inches to 5 feet from the outside to the inside of the back wall. The reason given for this is that longer grates cannot be served so well, and that in a larger burner the newly-charged ore forms too shallow a layer (the depth of the whole layer of pyrites, including

the partially burnt ore, is not in question here). I have, however, worked for a good many years with larger burners, nearly 6 feet from the front to the back end of the grate, and have burnt my ore better than the majority of other works using the smaller burners. To be sure, the usual 7-cwt. charge had to be all put in at once, whilst in the smaller burners it is put in in two halves every 12 hours; and many practical men assert that a 12-hours' is preferable to a 24-hours' charging; but this is not borne out by experience. It is, however, a decided mistake to try burning a much larger charge on the larger grate, say 8 or 9 cwt. This can only be done with poor ores, such as are not in use now-a-days, except locally; richer ores, especially those containing copper, are sure to be fluxed by the heat getting too high, and cause the greatest trouble. As a result of long experience, I am inclined to consider a grate-surface of 4 feet 6 inches by 5 feet 8 inches, and a depth of pyrites of 2 feet 3 inches, very favourable for burning 7 cwt. of 48-per-cent. Spanish ore, changing once every 24 hours.

The rate of burning just mentioned equals 30 lb. of 48-per-cent. pyrites per superficial foot of grate in 24 hours. With poorer ore (40 to 42 per cent.) I have certainly burnt in the same grate 8 cwt. (=35 lb. per square foot), and with 38- or 40-per-cent. ore even 9 cwt. (=nearly 40 lb. per square foot). In England the maximum quantity of pyrites burnt per square foot of grate will very rarely exceed 40 lb. of 48-per-cent. pyrites; reliable figures from one of the largest works are $35\frac{1}{2}$ and 39 lb. But in German works, according to Hasenclever, using Westphalian pyrites, the proportions are 41·6, 44·5, 57·8, 60·3, and 65·0 lb. (Wagner's *Jahresb.* 1871, p. 212). Bode (*ib.* 1874, p. 245) quotes for Westphalian pyrites of 41 or 42 per cent., 50·7 to 64·0 lb.; for Norwegian ore of the same strength, 38·3 lb.; for Valais ore, with 35 per cent. sulphur, up to 92 lb. per square foot in 24 hours. Favre (*Monit. Scient.* 1876, p. 271) states as the most favourable ratio in his experience 55·3 lb. of 40-per-cent. pyrites per square foot in 24 hours.

At the Oker works, according to Bräuning, the total grate-surface of eight burners belonging to a set of chambers of 65,500 cubic feet capacity amounted to 226 square feet—that is, 1 square foot to each 290 cubic feet of chamber-space, with a depth of 1 foot $6\frac{1}{2}$ inches pyrites over the grates. There are daily $3\frac{1}{2}$ tons of 40-per-cent. ores burnt, equal to 35 lb. per square foot of grate,

which agrees much better with my results than with those of Hasenclever and Bode.

It is hardly necessary to say that the pyrites-burners are always built in sets. Usually 12 to 24 burners are served by the same set of men; and they must be worked so that every one gets its regular turn, as is evident from the necessity of a regular evolution of gas. Frequently the burners are built underneath the acid-chambers. Not only must they in any case be protected against rain (if not underneath the chambers), but they must not stand in a space open at the sides, since strong winds would put their draught wrong, and cause them either to go too fast or to blow out at the doors. It is best to protect them by light walls or by a brattice with shutters adjustable according to the direction of the wind.

As the drawings of the English burners will show, each burner is independent of the other, and they do not communicate with one another, but only with the common gas-flue. Each burner, then, ought to have its own damper, which is not always the case. On the Continent, frequently the single burners are only separated by low walls; the ore in this case lies only about 18 or 20 inches deep on the grates, and the whole set is like one large burner with a divided grate. It is, of course, not possible, as on the English system, to treat each burner individually, to give it more or less draught, to isolate it for repairs, &c. Nevertheless this system is in favour with some of the more experienced Continental manufacturers, who say that 18 inches depth is quite sufficient for the rich ores now universally employed, and that the connection of the gas-space of all burners into one whole is preferable to the English system, because one burner can aid another and the whole is visible at one glance. Evidently this system answers its purpose as well as the English; and in a special case, in which I saw a set of English burners working alongside a set of burners of the kind just described, the manager informed me that he preferred the latter, because it was easier to regulate the draught than with the English burners.

The methods described in the patent of Hargreaves, Robinson, and Hargreaves (E. P. no. 5681, 1886) for treating pyrites are evidently less intended for the manufacture of sulphuric acid than for the recovery of arsenic, antimony, copper, silver, and gold. There is a whole set of burners combined in such a way that the air or the gaseous products at first formed can be successively

passed through them in regular rotation. The air, previously heated in recuperators, passes downwards, first through nearly exhausted ore, afterwards successively through ore containing more sulphur. The residual ore is treated with acid gases, in order to bring the metals into a soluble state. For details we must refer to the patent specification.

In Continental works possessing no Glover tower it is very usual to concentrate the chamber-acid up to 144° Tw. in *lead pans*, which are mounted on the top of the burners, and are heated by their waste heat. Of all plans for concentrating vitriol this is, as we shall see later on, the cheapest, only excepting the Glover tower. There is no reason why such pans should not be placed on the English burners as well; but even before the Glover tower did away with most lead pans, the above arrangement does not seem to have been practised in England. In this country, however, the space on the furnace-arch is otherwise usefully employed for drying "balls" from pyrites dust, &c. There are also, as we shall see in Chapter XI., sometimes reasons against placing the pans on the top of the burners.

The "*potting*" of the mixture of nitric and sulphuric acid (liquid nitric acid is not used in England for this purpose) has latterly nearly always been done in such a way that the burners are not disturbed by it. Even ten or twelve years ago the pots were frequently put on pillars between two burners, with a common gas-space; to these belonged special potting-doors in the burner-front, and cast-iron dishes as saucers for receiving the stuff that boiled over; these saucers had some fall towards the doors, so that the nitre-cake could not so easily run into the burners; but it got out of the doors, which made them look very dirty; and ultimately it also got into the burners themselves. None of the better factories have this arrangement now, but all pots belonging to a set of burners are placed in a separate "*nitre-oven*," which is nothing but an enlargement of the gas-flue, and either situated over the burners or on pillars outside the same. The latter is preferable; for also here there is always a metal saucer provided for catching the boiling-over nitre-cake: this may be cracked before it is noticed, and much nitre-cake may get into the burners, doing great damage. If the arrangement is similar to fig. 56 (where, by the way, the nitre-pots are replaced by a better contrivance to be described hereafter), no risk of the above-mentioned kind is run.

Favre ('Moniteur Scientif.', 1876) reports that the works in the south of France use pots of 2 ft. 7½ in. × 1 ft. 6 in. × 12 in., standing on a bridge between two burners; and he also mentions the drawback of boiling over into the burners. This would show that those works, even in 1876, were in a backward state.

We shall now give diagrams of different kinds of *pyrites-burners* such as are usual now-a-days in England. Figs. 53 to 55 show

Fig. 53.

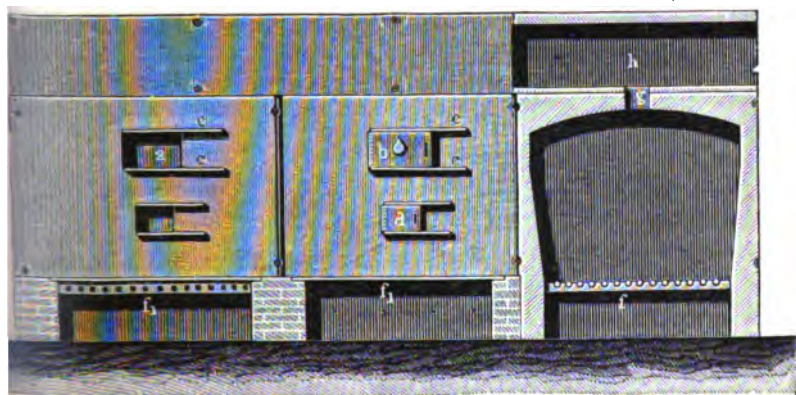
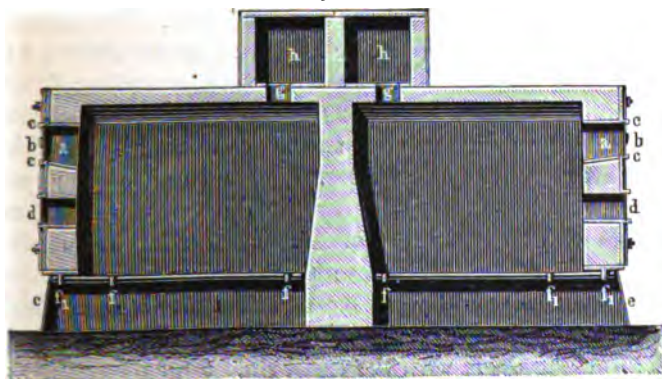


Fig. 54.

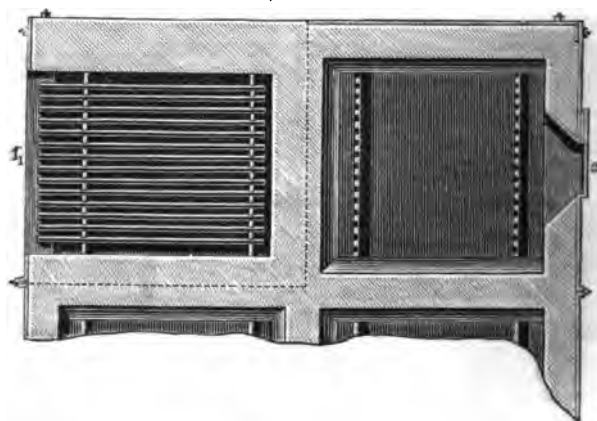


a simpler construction, which can be made with open sand castings; figs. 56 and 57 a more expensive kind of front plates, requiring planing, turning, &c.: the latter are much neater and cleaner, because no putty is required for the doors. Sometimes these front

plates undoubtedly become a little warped ; and then the doors are not tight without putty.

Fig. 53 shows two burners in front elevation and one in section, the first burner without doors. Fig. 54 is a cross section, showing two rows back to back ; fig. 55 a sectional plan, half taken just over the grate, half through the middle of a door. *a* is the working-

Fig. 55.



opening, with the door *b*, which slides in the grooved ledges, *c c*, cast to the front plate. The small door *d*, only to be used exceptionally, is arranged in precisely the same way. The openings of the brickwork inside are protected by small metal plates ; *e* is the movable cover of the ash-pit, provided with air-holes ; *ff* are the grate-bearers ; the front bearer *f1* at the same time carries the bottom plate for the front wall, and is perforated by round holes ; whilst *ff* are cut out in semicircles. The arches are sprung parallel with the working-doors, and, by the draught-holes *gg*, are in connection with the gas-flues *h h*. The latter, like the burners altogether, are cased in metal plates ; they are covered by fire-tiles.

A somewhat more costly but more perfect arrangement is shown in figs. 56 and 57, in front elevation and two sectional elevations. *a* is the working-door, with the small slide *b* for observing the interior of the burner ; it turns on hinges, and, as shown in fig. 57, lies on a projection of the front plate, slanting forward towards the bottom ; all the metal parts coming into contact are planed and faced, so as to close air-tight. Just in the same way the doors *c c*

for the grate and *d* for the ash-pit are made, whilst the rarely used doors *e* and *f* (the latter for the gas-flue) are made in the same simple manner as in fig. 53. The burners are supposed to be the last of the row; so that the nitre-oven *g*, with the semi-

Fig. 56.

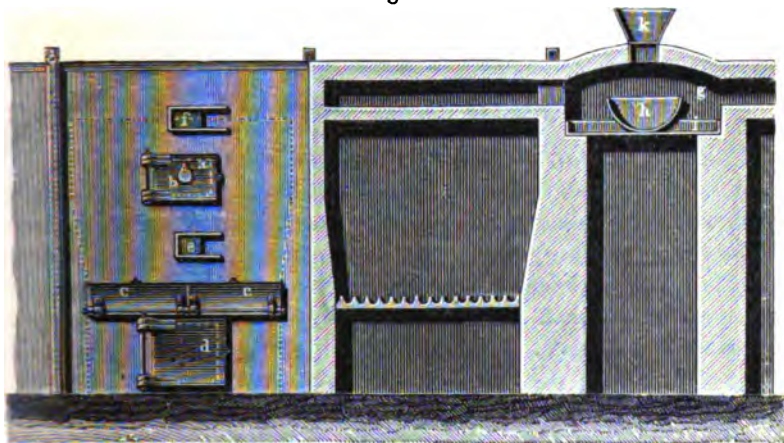
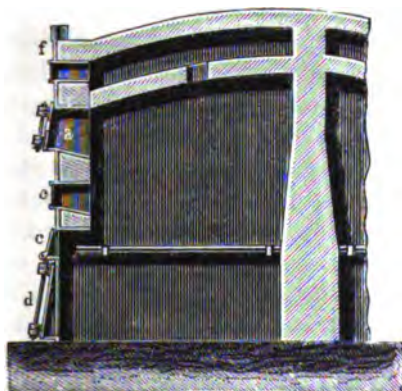


Fig. 57.



cylindrical trough *h*, the saucer *i*, and the hopper *k* are immediately joined to them. The diagrams are all on a scale of 1 to 50.

A remarkable pyrites-burner is that patented by J. & J. Addie (E. P. 180, of 1886). It consists of a cupola, brought to a white

heat, in which the pyrites is charged together with sandstone or other slag-producing material, and is burnt by a hot blast, the cinders being reduced to a molten slag which is run off from time to time. Unless this apparatus was intended for some very special purpose, not appearing on the surface, it must be pronounced as very impracticable from the standpoint of a chemical manufacturer.

Working of the Pyritea-burners for Lumps.

In order to *start a burner* it is first, if newly built, dried by a slow fire in the usual way, and then filled with burnt ore to within 3 inches below the working-door. If no burnt ore can be procured, ordinary road-metal, &c., can be taken, broken sufficiently to pass between the grate-bars when they are turned. The draught-hole of each burner is closed by a damper, and the working-door is left open. Then ordinary fuel (wood or rough coals) is heaped on the ore and lighted. After twelve or twenty-four hours the burner and the uppermost layer of the ore will have reached a dull red heat; the rougher parts of the fuel still present are then drawn out and an ordinary charge of green pyrites is put on. By the heat of the burner-walls, that of the ore below, and the fuel still present, the fresh ore will soon be lighted; when it is fully burning, the working-door is closed, the damper closing the access to the gas-flue is opened, and the gas allowed to go to the acid-chambers. Care must be taken in lighting up not to go too far, which would damage the burners.

Thus the process is started; and it is now continued regularly and uninterruptedly till it has to be stopped for external reasons. Repairs are very rarely necessary in pyrites-kilns; but those of other parts of the acid-making apparatus may compel their stoppage. At some few English works they put in the dampers every Saturday at midnight, and only open them at Sunday midnight; in the meantime all other openings are well closed; and the burner thus keeps its heat so well that the new charges at once take fire when brought in. If any temporary interruption of work does not last beyond four or six days, usually the burners can be kept hot enough in this way to be started without any fresh lighting-up by means of fuel.

The regular burning-process has a double object, from which

follow all the precautions to be observed. In the first place, the sulphur contained in the ore is to be burnt as far as possible; and, secondly, a just sufficient quantity of air is to be employed, no more and no less than is required for the chamber-process. This means, besides the air necessary for burning the sulphur to sulphurous acid, as much more air as is required for oxidizing the latter to sulphuric acid, and, moreover, a certain excess of air found necessary in practical work. Anyhow, therefore, the air will be more than just sufficient for burning *all* the sulphur contained in the pyrites; and the second condition seems thus to imply the first. But this can only be said for brimstone and for pure pyrites not containing any zinc blende or galena, &c.; for only the former can be desulphurized completely by their own heat of combustion. The sulphates of iron, which are always partly formed as intermediate products, are decomposed again at a comparatively low temperature into Fe_2O_3 , O, and SO_2 , or into Fe_2O_3 and SO_3 , for which the heat of the burners is quite sufficient. This is a little more difficult with the sulphides of copper; but the temperature of decomposition of CuSO_4 is also within a red heat. Moreover the copper-extraction works do not want all the sulphur to be burnt, but allow a residue of from four to at most six per cent. sulphur in the cinders. If, however, the ores contain blende or galena, which on burning are transformed into zinc and lead sulphates, the burner cannot possibly effect a total desulphurization; for these sulphates are only decomposed at a strong white heat, which is not allowable in a pyrites-burner, and they must thus remain as such in the cinders. Furthermore, if the pyrites contains calcium sulphate or carbonate, a corresponding quantity of CaSO_4 will remain in the residue. Any barium sulphate present would not be taken notice of in the testing of the pyrites or the cinders, being classed among the "insoluble."

In the case of the usual description of pyrites, not containing any considerable quantity of zinc or lead, the burning of ore in lumps will reduce the sulphur in the cinders with good work to 3 or 4 per cent. Less than 3 per cent. of sulphur very rarely occurs on an average of the whole year; but with very good ores it may go down to $2\frac{1}{2}$ per cent. Most frequently the limit stated above for good work is exceeded; some works leave 6 or 8 per cent. of sulphur, and even more, in their cinders, whilst their neighbours only leave 4 or 5 per cent. in the same ore.

The fault of this may be either with the description of burner employed or with the style of work. If, by the construction of the burner, the pyrites lie in too shallow a layer, and this is let down too soon on shaking the bars, it will easily come out badly burnt. But even if the burner is quite rightly built, much still depends upon the skill and care of the burner-men.

Excellent results are obtained with some of the very rich descriptions of Spanish non-cupreous pyrites, recently come into the market (p. 46). These pyrites can be burnt down to 0.5 per cent. of sulphur in the cinders, so that the latter can be sent straight to the blast-furnaces. But if this degree of purity is to be obtained, the place in front of the kilns, where the burnt ore is drawn out, must be kept perfectly clean, so that no green ore can get mixed among the cinders; and any portions of these which have been spilt from the discharging bogies on to the ground must not be shovelled back into these, as they will have some admixture of dust from green ore, but they must be put back into the kilns.

How much depends upon employing the ore in *neither too large nor too small pieces*, and upon keeping the pieces of as *uniform a size* as possible, has been mentioned on p. 208. Only then it will be possible to regulate both the depth of layer and the draught in a satisfactory way.

Whether pyrites is properly burnt or not can be recognized to a great extent by the eye. By the burning-process the pieces swell out and burst in some place; they become light and porous, and assume the red colour of ferric oxide, in the case of cupreous pyrites a more blackish-red colour. The burnt ore ought therefore to consist of light porous pieces of the proper colour, apart from the powder always present in large quantity, which is generally sufficiently burnt off. Already, on taking up the larger pieces, their weight will allow a rough judgment of the state of the burning; and this can be more distinctly recognized by breaking the pieces and observing whether they contain a raw core in the centre. Also the presence of many slags (scars) on the cinder-heap is a proof of bad burning.

Important as these empirical signs are, no well-managed factory will be satisfied with them, but will from time to time, daily or at least twice a week, have the cinders tested, after having drawn a large sample and reduced it properly. At all events the above-mentioned empirical signs have hardly any value for small ore.

The chemical testing of pyrites cinders (burnt ore) can take place by exactly the same methods as described in the second Chapter for the analysis of pyrites itself. We have seen there, that in the case of burnt ore more expeditious methods may be used, and that among these that of Watson (igniting with sodium bicarbonate and titrating the undestroyed sodium carbonate) seems to be the most accurate (p. 63).

The sulphur contained in the burnt ore is no longer in the shape of FeS_2 , apart from any quite raw cores in large pieces. But even fine or quite porous cinders, burnt as well as possible, also those from pure pyrites free from lead, zinc, and lime, always contain sulphur; and as this cannot be in the shape of FeS_2 , the question can only be whether they contain FeS or sulphates of iron (most probably basic ferric sulphates), or both. According to Scheurer-Kestner and Rosenstiehl (Bull. Soc. Chim. 1868, ix. p. 43), the cinders contain essentially FeS ; they give two analyses—(i.) of properly burnt ore, (ii.) of an operation carried on too hot, so that the ore had fluxed. Both are from Sain-Bel pyrites, containing 46.1 per cent. sulphur in the pieces and 49.28 in the smalls.

	I.	II.
Moisture	1.0	
FeS.....	8.5	27.2
Fe..... 5.4	}	17.3
S 3.1		
		9.9
Oxide of iron.....	72.0	62.4*
Fe..... 50.4	}	41.0
O 21.6		
		21.4
Quartz	18.5	10.4
	<hr/>	<hr/>
	100.0	100.0

According to these analyses, there would be no ferric sulphate whatever in the residues, which is very improbable, as such can be proved by washing with water (comp. Bode, Dingler's Journal, cxviii. p. 327, and further analyses by Phillips, Gibb, Bräuning, Wedding, and Ulrich in the Chapter treating of the recovery of copper from the cinders).

* The calculation does not agree here; 62.4 Fe_2O_3 would contain 43.68 Fe.

Richters (Dingl. Journ. cxcix. p. 292) gives the following analysis of burnt ore from the Silesia works at Saarau :—

Water	4·35
Iron	43·36
Manganese	0·16
Silica	13·92
Alumina	4·84
Lime	0·02
Zinc oxide	8·83
Sulphur trioxide	4·35
Sulphur.....	1·53
Oxygen and loss	18·64
Nickel and arsenic	traces
	<hr/>
	100·00

Phipson has published the following analysis of residue from Irish pyrites (Chemical News, vol. xviii. p. 29) :—

Zinc oxide	5·50
Cupric oxide.....	2·86
Manganese oxide	1·60
Nickel and cobalt oxide	0·12
Cadmium oxide	0·01
Lead oxide	1·67
Antimony oxide	0·04
Ferrous oxide	1·17
Alumina	3·25
Sulphur	2·60
Thallium	traces
Indium	traces
Gangue	15·00
Ferric oxide	65·99
Lime	0·11
Magnesia	0·08
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	100 00

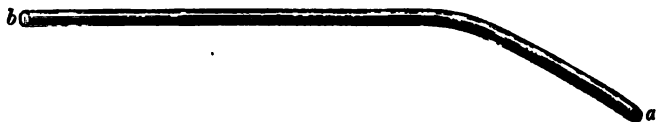
Everything that has been said on the maximum of sulphur in the cinders to be aimed at, only refers to the burning of pyrites proper—that is to say, of ores containing essentially FeS_2 , and got

exclusively as a raw material for vitriol-making, in which case the cinders are as good as worthless. Just in the same line are those cupreous pyrites (with up to 4 per cent. of copper) whose copper can only be extracted by the wet process; for these the above-mentioned rules for the sulphur in the cinders are equally valid. But the case is quite different with a number of ores where the residue from the burning is regarded as by far the most important product, and where the gas is only a by-product, often only converted into sulphuric acid in order to get rid of it. To this category belong blende, copper-pyrites, coarse metal, &c. Here the burning-down to the above-mentioned minimum of sulphur is partly not possible, partly not even desirable (as for copper-pyrites); and there exist for each case definite rules, which, however, do not belong to the domain of acid-making, but to that of metallurgy. Even where a larger percentage of sulphur is required for further metallurgical operations, it is more rational from the standpoint of the acid-maker, in order to save labour, burner-space, &c., to burn the material as well as possible, and to supply the necessary sulphur afterwards by adding a little green ore; thus, for instance, the copper-extraction works proceed when they receive the cinders too far desulphurized. The case of zinc blende is a special one and will be treated of hereafter.

We now pass on to the second fundamental condition of proper work in the pyrites-burners, viz., *that neither too little nor too much air be employed*. At this stage we leave out of consideration the absolute quantity of air required, and only treat of the practical rules and of the appearances observed in the burners themselves. If too little air is admitted, whether from too few holes in the bottom door being opened, or from the damper in the draught-hole not being enough drawn, or because the pipes are stopped up with dust, or the draught in the whole chamber system is insufficient from one cause or another, the same thing will happen as with sulphur-burners when they get too hot: sulphur will sublime as such, and will be deposited in the flues, the dust-chambers, the Glover tower, or the chambers themselves. It is, however, a more frequent and serious consequence that, in the case of insufficient draught, the often-mentioned *slags* or *scars* are formed. These, as Scheurer-Kestner and Rosenstiehl have shown (*l.c.*), consist mostly of *iron monosulphide*, FeS , which is necessarily formed when FeS_2 is heated with exclusion or insufficient supply

of air, along with free sulphur. It is easily fusible, and fluxes in the burners to more or less large cakes or scars, upon which the air has practically no action. The FeS fluxes all the more easily, as in the case of insufficient supply of air, where no cooling by the excess of air takes place, more heat is developed in certain places than when the supply of air is abundant. The scars mostly enclose some green pyrites, and in this way cause a further loss of sulphur. A much greater loss is occasioned by their stopping the passage of air, so that the ore above and below a scar is very incompletely burnt. The heat is locally increased and driven further down than it ought to be; the zone of combustion is removed further downwards; and on letting down the ore the pyrites partly comes out incompletely burnt. If scars have formed in the burner, they naturally descend as the cinders are let down, and they would ultimately lie immediately on the grates and entirely stop them up. This, however, must be prevented by all means. A careful workman always breaks up the surface of the old ore before putting in a fresh charge; and thus he finds out whether any scars have formed, which mostly takes place near the surface: they can then be easily brought to the surface by means of hooks and pulled out at the door. But if they have been overlooked at first and have got lower down, in doing which they constantly increase in size, their removal is more difficult. Then a very large and heavy poker of the best tough iron (these are made up to 12 feet long and 2 inches thick), bent in the way shown in fig. 58, is introduced into the

Fig. 58.



burner through the charging-hole, and the men work it till they have got the point *a* underneath the scar. Several men, working at the end *b*, then try to lift up the scar, in spite of the resistance of the superjacent mass of pyrites. This labour is very disagreeable, exhausting, and difficult. The middle doors, between the charging-door and the grate, found in all pyrites-burners, are only used in extreme cases.

With the low burners mentioned on p. 227, where the ore lies

only at a depth of 20 inches, scarring is next to unknown, at least if the ore is very carefully sized, so that all passing through a $\frac{1}{4}$ -inch riddle is kept out. This agrees with the facts which will now be explained.

Apart from other causes, the supply of air in a burner may be insufficient because the ore lies too deep. As the depth of the ore depends upon the vertical distance between the grate and the working-door, it follows that for ores behaving very differently in this respect differently built burners must be used. Thus the deep burners built for Irish pyrites had at once to be given up when Spanish pyrites began to be used. With the same height of pyrites which was just right for the poor ore, in order to keep the heat better together, the rich cupreous ore, in itself more fusible, became far too hot, and, moreover, the air could not pass through quickly enough to make a *complete* burning of the ore possible at every point; from both causes combined followed this effect (easily comprehensible after what has just been said), that the scarring became excessive. It is always much more feasible to burn poor ore in a shallow than rich ore in a deep burner. Insufficiency of draught, if very considerable, will be easily recognized by the gas blowing out of all the joints of the burners, and especially coming out in force whenever the working-doors or the bottom door are opened. On the other hand, the draught is not to be so strong that too much air will get into the chambers; the gas ought to be kept as rich as possible, as will be shown hereafter. It may be assumed that the draught is just right, if, on opening the small slide in the working-door, neither gas nor flame issues from it, nor, on the other hand, the flames inside the burner perceptibly tend towards the draught-hole. They ought to rise up perpendicularly and quite steadily; and on opening the door they may even tend slightly towards it. As, however, the exact regulation of the draught can only be effected by regulating the holes in the bottom door, and as on each opening of the doors above or below the grate much more air must get in than is necessary, of course the times during which the doors are opened are restricted as much, and the charging, shaking of the grates, and discharging are managed as quickly, as possible. It is very advisable to close the holes in the bottom door completely while the top door is open. If the draught is not very abundant, whenever the door is opened, there will be no room for so much air rushing in, in consequence

of which a portion of the gas will rush out and get into the burner-house; this is both a loss and a nuisance to the workmen, and, in greater quantity, also to the neighbours.

For regulating the supply of air several plans are possible. The regulation takes place either *before* the grate, by the holes in the bottom door, or *behind* the grate, by means of the damper in the draught-hole or that in the large chimney behind the chambers. The latter is only available where all the burners have a common gas-space; otherwise the draught through the chimney must be equal to the maximum amount required for all the burners, and must be changed according to the atmospheric conditions, each burner being regulated separately. This could be done best and most safely by the dampers in the draught-holes connecting each burner with the gas-flue; but these are rarely used for this purpose; they would have to be made very tight-fitting, and then would easily be set fast by flue-dust. Therefore here also the draught is made sufficient for all eventualities. The real regulation of the air, at least generally in England, takes place by means of the holes in the ash-pit door, of which a sufficient number are closed by plugs or otherwise. Scheurer-Kestner went so far as to pass all the air through a Combes' anemometer; but this can only have been done for isolated experiments, since such a delicate instrument can hardly have been kept fit for use for any length of time in an atmosphere thus exposed to acid vapours and to dust. It is therefore left to the burner-men to open or close the holes in the door as required.

The supply of air is usually regulated by the following practical rules:—At the beginning (that is, immediately after making a fresh charge) the burner does not want very much air, till the ore has caught fire, which will take half an hour or an hour. Then more air must be admitted, always with the above-mentioned restriction—that the flames rise perpendicularly, and tend slightly towards the slide when this is opened. When, however, the principal portion of the sulphur is burnt and the flames become scarce, the air is altogether shut off, and further action is left to the heat of the burner. About two hours before it is time for recharging, the working-door is opened and the ore is well raked and turned over by means of a hook to a depth of 3 or 4 inches, and any small scars are removed. If herewith blue flames appear to any extent, this proves the burning not to have been sufficient, and a little air

must be admitted. When the whole time is up, be it a twelve-hours' or a twenty-four hours' turn, the air is entirely shut off at the bottom, the small doors covering the grate-bars are opened, and these are turned two or three times, leaving each alternate one out. During this the workman must look through the working-door, to see whether the layer of ore is let down evenly all over; he can easily manage, by the judgment of the eye, not to let the ore down too much or too little. Then, as quickly as possible, the new charge of ore in pieces (usually with a little dust), which must have been lying ready in front of the burner, is put in, and the process begins again. It is evident that there must be a regular rotation, so that a fresh burner comes in turn every hour or so; this is both indispensable for a regular evolution of gas, and convenient for distributing the labour over the day.

The burner-men ought to shake the grates quite equally for the purpose of discharging, so that the ore does not come down more quickly in one place than in another, and to take care that only cold, thoroughly exhausted cinders, but no red-hot ore, comes down. They ought then to work up the ore on the top through the doorway with their pokers, and rake the surface so as to make it even again. Then they must charge the new ore equally all over, starting about two inches towards the door from the back and the sides. Two men can attend to a set of 18 or 20 burners, consuming from 6 to 8 cwt. of pyrites each every 24 hours, including the wheeling away of the cinders and the potting.

The interior of a burner, after the throwing-in of a fresh charge, is, of course, at first quite black. Gradually small blue flames appear, which become larger and more lively and cover the whole mass. After a few hours they become scarcer again; but the mass in the meantime has become red-hot. Later on it cools again; and towards the end of the period there is no glowing visible at the surface; but as soon as the mass is stirred up, the glowing appears again.

The men like to employ a practical test, to convince themselves that the burner is not too hot for recharging, in the shape of strokes made with brimstone on the burner-door: so long as these take fire at once, the burner is still too hot; only when they remain is it cold enough for charging. Frequently it is necessary to wait a little, even for a few hours, after shaking the grate-bars and letting down the burnt ore, in order that the burner may

cool a little before recharging it; this has the advantage that the top layer, by turning it over, is caused to burn its sulphur more thoroughly than it can be burnt after cold pyrites has been thrown in.

Generally it takes some time before the men get used to a new kind of burner or of pyrites. If even skilled men are taken from other places, they require special supervision, and still more if a new kind of pyrites has to be tried. If at all possible, different kinds ought not to be tried mixed up, but one kind adhered to for some time, because only in this way do the men get used to a thoroughly proper treatment of the burner. Each kind of pyrites requires a little different treatment as to supply of air, to breaking up, &c.

An extremely important assistance in regulating the burning-process is the analysis of the gas, which, however, is nearly always made for a whole set of burners together in their common flue. We shall enter into the details of this later on.

If a pyrites-burner is working properly, it will, if touched outside, be so hot in its upper part (say 6 inches below the working-door) that the hand cannot be borne upon it; further down it must be cooler; and immediately above the grates it ought to be cold, or at most hand-warm. *This is one of the most important practical signs of the proper working of the burner.* If a burner is too hot below, this may be the consequence of insufficient draught, or (which in the end comes to the same thing) there has either been too much pyrites charged or there is too much dust in the burner, which has stopped up the interstices. Too much dust may come from bad riddling, from too much having been added on purpose, from the falling of the "balls" inside the burners, or from the decrepitation of "explosive" ores (comp. p. 46).

In any case, the first thing to be done, apart from doing away with the cause of the evil, is to *cool* again the excessively hot burner. Above all, *more air* must be admitted; and, in order to drive up the heat more certainly, the new charge must be kept back a little,) and the fresh ore not put at all in the middle, but only along the sides and the back of the burner. It always takes one or two days, sometimes more, before a burner has recovered its normal temperature. In specially obstinate cases there is nothing for it but making very small charges for a day or two, till matters have come right again. Some manage by taking out

the ignited top layer, allowing it to cool a little, and putting it back into the burner, which in the meantime has had more draught, owing to the lower depth of ore, and thus has cooled itself.

If a kiln is allowed to go too hot for any length of time, whatever may be the cause of it (want of air, too large charges, stopping up by dust, bad breaking up), the consequence will always be the same, viz., increased scarring up, with all its unpleasant accompaniments. I have had to deal with cases where the scars became so copious that the burner had to be put out, the grates had to be drawn, the whole of the stone taken out, and the burner freshly filled up.

Of course it also happens sometimes that a burner goes *too cold* and the fresh charges take fire too slowly. This may be caused equally by a want of draught or by too small charges, and can be easily remedied in this case. If it has, however, got so far that the new pyrites will not take fire at all, nothing remains but putting in very hot ore from some of the other working-burners; in this way the matter may always be put right with some patience, unless large scars are lying on the grates, or there are other serious faults, which must be done away with before the burner can be expected to work properly. A frequently used but objectionable remedy against cold burners is putting live coals on the pyrites. Carbonic acid is a great enemy to the chamber process, probably not so much by diluting the gas (for its injurious action is far too great to be attributed to that alone), as by lying in the lower part of the chambers and preventing contact between the chamber-gas and the bottom acid, till it is removed by diffusion. This point, however, is not yet cleared up.

A pyrites-burner may also go too cold if there is *too much draught*—if, therefore, besides the air required for its intense working there is an excess, which only acts as inert cooling gas. This is a very great fault; for in this way the consumption of nitre is increased and the yield of sulphuric acid very much diminished. Long before the burners cool from this cause, an excess of air may become injurious in this way; and by observing the flames in the burners (much better, however, by the analysis of the gas), it must be ascertained whether the proper proportion of air is present or not.

Balard reports ('Rapports du Jury International,' 1867, vol. vii.

p. 29) that in the first trials of Perret and Olivier for employing pyrites in manufacturing sulphuric acid, they at last succeeded in properly conducting the combustion, but obtained a very small yield of acid. They ascribed this to an insufficient draught, and applied a fan-blast; but the yield instantly became minimal. Now the other extreme was tried; the air-channels were quickly stopped up with boards covered with sheep-skins and fastened by stays. At once the chamber process became regular, and the key to employing pyrites in the manufacture of sulphuric acid was found. Probably the previous endeavours of Clément-Desormes in this respect were frustrated by his allowing too much air to enter.

Some have objected to the employment of *damp* pyrites (Kerl-Stohmann's 'Chemie,' 3rd ed. vi. p. 197), because in this case, on burning, more sulphates are formed, which give off sulphur trioxide; this takes up moisture, and condenses as sulphuric acid before getting into the chambers, destroying the flues and so forth. Even with dry ore in damp weather similar phenomena are said to be observed, and a smaller yield is said to be the consequence of the moisture in the air. I, on my part, have never noticed such an effect of damp weather, nor have I been able to learn anything about it elsewhere, in spite of numerous inquiries. It would be desirable to examine this point specially. The formation of sulphur trioxide, as well as the occurrence of liquid sulphuric acid, in the connecting-tubes, certainly has been established; but that the moisture of the air acts in a way to increase that formation, has not yet been proved.

He who has no practical acquaintance with the matter, looking at these numerous sources of mishaps, may be inclined to think that the working of a set of pyrites-burners is a most difficult task. But it is far from that. If once the burners are in order, they remain very long so if the burner-men know and perform their duty to any considerable extent, and if proper supervision is exercised over them; the pyrites-burners then give even less trouble than sulphur-burners. To be sure, when they do get wrong, it takes energetic and experienced management to put them right again.

It will now hardly be necessary to explain in detail why there are only narrow limits for each given burner and style of charging, within which the *quantity* of pyrites charged may vary. If too much is charged, the burner scars; if too little is taken, it gets

cold. When, therefore, for any reason the daily quantity of pyrites has to be cut down, it is necessary to put out a corresponding number of kilns and to fully work the remainder. Only in the case of brief temporary interruptions is it possible to charge rather less than usual for a few days; but I would recommend even in this case rather to allow the bulk of the burners to go on as usual, and to keep the necessary number hot without fresh charges by closing all openings. Then these kilns will be much more easily put in order by the assistance of the other burners in full work than if they had *all* cooled down.

3. BURNING PYRITES-SMALLS.

We have seen above (p. 208) that the fine powder which passes, say, through a $\frac{1}{2}$ -inch or at most a $\frac{3}{4}$ -inch riddle must be kept out of the ore going into the ordinary pyrites-kilns. The "smalls" or "dust" produced in this way, whether it be on breaking the ore at the works or already at the mine, must be dealt with separately.

This can be done in very different ways, according to circumstances. Where pyrites-smalls are not bought as such, the question is only about the dust arriving along with the bulk of the ore and about that made in breaking. Much more dust is made when breaking by machine than by hand—in the former case up to 20 per cent. with middling hard ores, and even more with soft ores. Formerly, before rational and really satisfactory contrivances for the burning of smalls were known, some large works, which had already mounted Blake's stone-breaking machine, went back to hand-breaking, in spite of its costing three to six times as much, merely in order to avoid the excess of dust. This was especially the case with works using soft ores, such as the Tharsis ore; with Norwegian ores the advantage was always on the side of the mechanical breaking, because these are much harder and make less dust. If the quantity of dust going through the smaller riddle does not exceed $1\frac{1}{2}$ cwt. to the ton, it can be got rid of, according to my own experience, without any special contrivance, in the following way:—The dust is sifted off as usual, and a certain quantity of it is laid down for each burner alongside the pieces. If, for instance, the whole charge is 7 cwt., $6\frac{1}{2}$ cwt. of pieces are used and $\frac{1}{2}$ cwt. of dust; if more than this is used, the

burner easily gets out of order. First the coarse ore is charged as usual; and then the man throws the dust with his spade along the *sides* and the *back* of the burner, leaving the whole central part free. Anyhow, the ore ought to be levelled with a hook, after throwing in the charge, in such a way as to make it higher along the sides and back than in the centre of the burner. The reason is this: the air entering from below meets with much less resistance at the comparatively smooth walls than in the centre of the layer of ore, and it will preferably rise along the former; the centre thus will get less air than the parts next to the walls. If, however, the latter lie at a higher level, and especially if the passage of air is obstructed by the dust lying at those places, the draught will be more nearly equalized, and the burning will take place evenly all over the area of the burner. Of course it is not well to proceed too far in this way.

The arrangement just described does not suffice if more than $1\frac{1}{4}$ cwt. of smalls to the ton of pyrites has to be dealt with; and special arrangements must then be resorted to. Probably the oldest method, now almost obsolete, was the following:—The small ore is, without further grinding, mixed with sufficient clay to make it plastic, made into a puddle with water, formed into *balls*, and dried on a steam-boiler or pyrites-burner. Rarely less than 10 per cent. of clay will be required for this, often more, up to 25 per cent. The balls are then charged along with lumps into the ordinary burners, but never too many at a time (at most one sixth part of the whole charge), because they fall to powder in the burner after a time, and if used in a greater proportion would stop the draught. Only locally is such rich clay found that the balls stand pretty well in the burners and can be well burnt off. The workmen dislike them very much, because they disturb the working of the burners, even when the above-mentioned restriction of their quantity is observed; if a burner is not quite warm, they must at once be left off. Some, in order to get rid of them without disturbing the burners, burn them by themselves, mixed with “coal brasses,”—that is, the pyrites picked out of coals, which always retains some of the latter, and therefore burns more vividly and gives out more heat than pure pyrites; but then it sends the injurious CO_2 to the chambers. Usually not much is gained by making the balls with clay, since they so quickly fall to pieces in the burner; and nearly as much can be done by throwing the

dust at once into the burner and saving the cost of making the balls. Only by a very strong admixture of clay can the disintegration of the balls be prevented; but then the loss of sulphur and the contamination of the burnt ore is all the greater. In both cases the sulphur left in the burnt ore rises very much, from 6 to 8 per cent. and more. Where the cinders go to copper-extraction works, these usually prohibit the use of clay for balls.

These clay balls are connected with so many drawbacks, that something else was soon looked for. This was indispensable where nothing but smalls could be obtained, or where they could be procured so cheaply that acid-makers wished to dispense entirely or partially with using lump ore. At the pyrites-mines there are usually enormous heaps of smalls, which formerly were not saleable at all and would sometimes have been given away for nothing, just to make room. In other places pyrites only occurs in a loose, roughly crystalline shape; and, again, in others it is obtained by wet preparation altogether in the state of smalls. Thus there was great encouragement for constructing apparatus for burning small pyrites in large quantities.

The contrivances for burning pyrites-smalls may be divided into three classes, namely, those working by external heat, those utilizing the heat of ordinary burners for pyrites in lumps, and those arranged for burning the smalls by themselves without any extraneous apparatus.

(a) *Burning Pyrites-smalls with the help of Coal-fires.*

Apart from the use of "balls," the oldest plan of dealing with pyrites-smalls is that of spreading them on the bed of a furnace, heated by flues underneath, the fire-place being arranged at one end and the pyrites-dust being introduced at the other, and being gradually moved forward towards the fire end, as room is made for it by drawing out the burnt ore. In thus being turned over many times on its way from one end of the furnace to the other, the sulphur was supposed to be thoroughly burnt. This is, however, but imperfectly the case, even if the furnaces are made 100 feet long. Moreover, the cost of fuel in the best case is very heavy (at least 10 cwt. of coal is consumed for a ton of pyrites, usually much more), so is the cost of labour; the continuous opening of the working-doors caused very much false air to get into the chambers, even fire-gases sometimes leaked

through the furnace-bottom, and therefore the consumption of nitre and the yield of acid were very bad. We shall, consequently, not go into any details about these "muffle-furnaces," but refer to the first edition of this work, where, on pp. 186 to 190, the Belgian furnaces, and those of Spence, of Godin, of Imearry and Richardson, are described and partly illustrated by diagrams. Since it has been recognized that no extraneous heat is necessary for burning pyrites-smalls, such furnaces must be looked upon as altogether irrational, and they are practically obsolete now. This, of course, has nothing to do with the fact that similar furnaces are in use for roasting galena and other ores which do require external heat for the purpose.

(b) *Burning Pyrites-dust by the heat of burners for Lumps.*

This was considered a great improvement upon the older methods, but it must be equally pronounced obsolete now, at all events in the case of ordinary pyrites. We shall therefore treat these processes also very briefly, referring for details to the first edition of this work.

The first furnace for burning pyrites-smalls by means of the heat from lump-burners seems to have been that patented in France by Usiglio and Dony, Jan. 24, 1852, which, however, did very imperfect work. Much more important is the furnace constructed by Olivier and Perret, which was introduced into the majority of French works and was in use there for many years, until replaced by the Malétra burner (*vide* p. 252). Olivier and Perret place above an ordinary lump-burner a number of shelves made of fire-clay, and charged with a thin layer (not above $\frac{1}{4}$ inch) of pyrites-dust (for exact description and diagrams, *vide* first edition of this work, pp. 193 to 196). In this way it is possible to burn about 1 cwt. of dust to each 2 cwt. of lumps, the sulphur in the cinders being reduced down to 4 or 5 per cent. The whole furnace was originally about 20 feet high, which necessitated a second working-stage above the ground. There is, of course, a good deal of labour connected with this system. Later on it was made less high, and so arranged that all the doors were on one side, so that a number of furnaces could be grouped into a set.

In a simpler form, namely, that of a single cast-iron plate above ordinary lump-burners, this system was introduced into some

Tyneside works, first by MacCulloch, but was soon abandoned again (comp. 1st edition, pp. 191 to 193).

Another way of carrying out the same principle was the furnace of Hasenclever and Helbig (1st edition, pp. 196 to 201). Here, at the end of a set of lump-burners, a tower-like apparatus was arranged with eight inclined shelves of fire-clay, over which the dust was gradually to slide down and to be burnt on its way. Thus from 10 to 16 cwt. of smalls were to be burnt for each 48 cwt. of lumps; but the principle of automatic sliding down did not answer; the motion of the dust had to be aided by hand-work, with much introduction of false air; and although a large number of these furnaces were erected, principally in Germany, they have been almost or entirely abandoned for some time past.

(c) *Burning Pyrites-smalls without external heat.*

We must, in the first place, mention a plan which does without any special dust-burners, and only represents an improvement in making "balls." It is based upon the fact that pyrites, if it is in the shape of very fine powder mixed with water, coheres to a solid mass *without the aid of any plastic substance*. This is caused by the fine pyrites-dust, in the presence of water and air, beginning to oxidize very soon, even at the ordinary temperature; thus basic ferric sulphate is formed, which firmly cements together the separate grains of dust. This result only takes place to a sufficient extent if the grains of dust are very fine and the mixture with water very perfect; and this can never be attained by merely sifting and moistening the fine ore. The ore must therefore be ground finely with water in a mill, for which purpose usually the so-called *pug-mills* are used, a kind of vertical mortar-mill, sometimes with revolving bottom dish, or, if the dish is stationary, with a mechanical arrangement for throwing out the mixture as soon as it has reached the proper consistency. The pyrites-small are thrown into the mill, water is run on, and the mill is run till a homogeneous mixture similar to fine mortar has been formed, which by itself has somewhat plastic properties. This mass is dried in layers of $\frac{1}{2}$ inch thickness on the top of the pyrites-burners, often in cakes about 18 inches square; and after twenty-four or thirty-six hours it has hardened sufficiently for use. It is broken up into pieces of the same size as the lump ore, and charged along with this into ordinary pyrites-burners. In this it is not

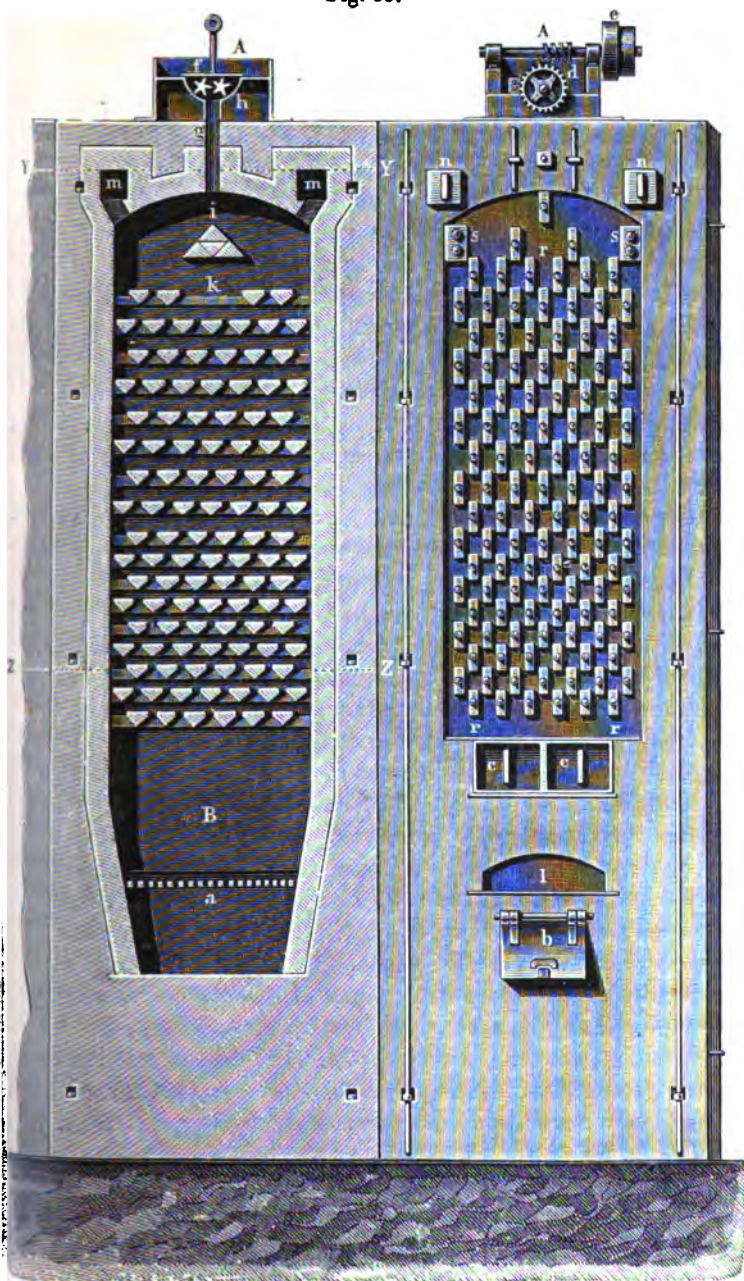
necessary to observe a certain proportion ; for the balls made in this way are so hard that they can be thrown to the ground without being broken, they do not fall to powder in the burners, and burn out as well as lumps ; their cinders are, of course, of the same value as those from lump ore, whilst those mixed with clay make the utilization of the ferric oxide, at last obtained at the copper-extraction works, very difficult.

The principal drawback of this process is this, that the mills suffer very much wear and tear from the hard pyrites. In spite of this, it is still the most usual in the large English works. The labour of grinding, carrying to the top of the burners for drying, taking down, breaking up, and laying down in front of the burners amounts to 1*s.* 4*d.* per ton. To this must be added 6*d.* for coals for working the mill, and wear and tear of the same, altogether about 2*s.*, apart from the wages for the burning itself (another 2*s.* per ton).

The same result as is attained by the "pugging" process is obtained in perhaps a more complete, but decidedly far more costly, way by the process of H. Wurtz (U. S. Pat. 252, 287). He mixes the fine ore with powdered metallic iron, moistens this with a solution of sulphate of iron, and allows the whole to agglomerate by rusting.

The process just described is not applicable in cases where the great bulk or the whole of the pyrites employed is in the shape of dust. In such cases formerly the only available contrivance was the above-mentioned muffle-furnace, with all its great drawbacks. The first who proved that the heat generated by the combustion of ferrous bisulphide is sufficient for keeping the process going without any external aid, quite as well in the case of pyrites-smalls as in that of lumps, was Moritz Gerstenhöfer, whose furnace is described at length and shown in several diagrams in the first edition of this work, pp. 205 to 215. We give here only one diagram, fig. 59, and a short description. It is a shaft, 17 feet high, 2 feet 3 inches long, and 2 feet 7½ inches wide inside, provided with a large number of prismatic fire-clay bars, so disposed that the intervals of each upper tier are covered by the bars of the next lower tier. The pyrites-dust is fed in by means of fluted rollers, and drops from tier to tier, forcing down the particles previously lying on the bars according to the natural slope of the ore. Before starting the feed of the ore, the furnace is brought to a

Fig. 59.



bright-red heat by means of a coal-fire. Afterwards the combustion of the pyrites by means of the air entering from below is quite sufficient for keeping up the heat.

The two great drawbacks of the Gerstenhöfer burner are: the very large amount of flue-dust produced in it, and the very incomplete desulphurization of the ore. Principally for these reasons this ingenious furnace has been abolished again nearly everywhere, and is now only used for roasting "coarse metal" in one or two copper-works, and at the Freiberg works for a variety of mixed ores. It may be stated generally that it is well adapted to ores or metallurgical products containing from 25 to 36 per cent. of sulphur. Below 25 per cent. it does not work; above 36 per cent. it is far inferior to the shelf-burners to be presently described.

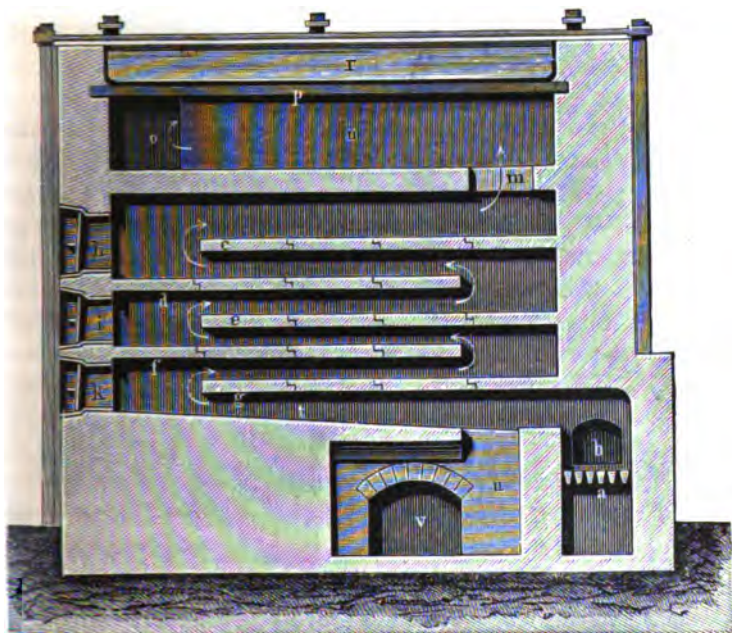
According to Scheurer-Kestner (Bull. Soc. Chem. xlv. p. 228), Perret has recently constructed a furnace, resembling Gerstenhöfer's, but free from the defects of the latter. The pyrites is said to be thoroughly utilized and the cost of labour reduced to one-half as against Malétra's "shelf-burners" (see below). At the time of Scheurer-Kestner's report the furnace in question was evidently still in the experimental stage; and as nothing more has been heard of it, its success cannot have been so great as anticipated.

The object but imperfectly attained by Gerstenhöfer's invention has been realized by a very simple plan—so simple, indeed, that it was not thought worth patenting at the time, although it has subsequently proved to be of immense importance. Mons. Malétra, owner of the works of Petit Quevilly, near Rouen, after having for some time burnt his smalls by means of an Olivier-Perret furnace, conceived the idea of separating the upper part of this furnace from the lower, and working the dust by its own heat of combustion without any aid from a lump-burner. This idea, which was worked out about 1867 with the aid of M. Tinel, proved entirely successful; but in spite of this, and in spite of this "*shelf-burner*" being the simplest and cheapest of all dust-burners, it became comparatively slowly known; but since 1873, when it became better known by the Vienna Exhibition, it has spread on the Continent with extraordinary rapidity, whilst for a long time it attracted little attention in England. The first burner out of France seems to have been erected at the works of Schnorf Brothers, at Uetikon, near Zürich, in 1870; in Germany the first was erected at Kunheim's works in Berlin. Even if, as it would seem, some form of

these simple shelf-burners had been previously in use here and there, their *successful* application for burning pyrites-smalls seems first to have been effected by Malétra's works.

Fig. 60 gives a longitudinal, fig. 61 a cross section, the latter through two furnaces. Usually a whole set is built in a row. In order to start it, a coal-grate, *a*, and fire-door, *b*, are provided, which are walled up when the burner has got up to a white heat.

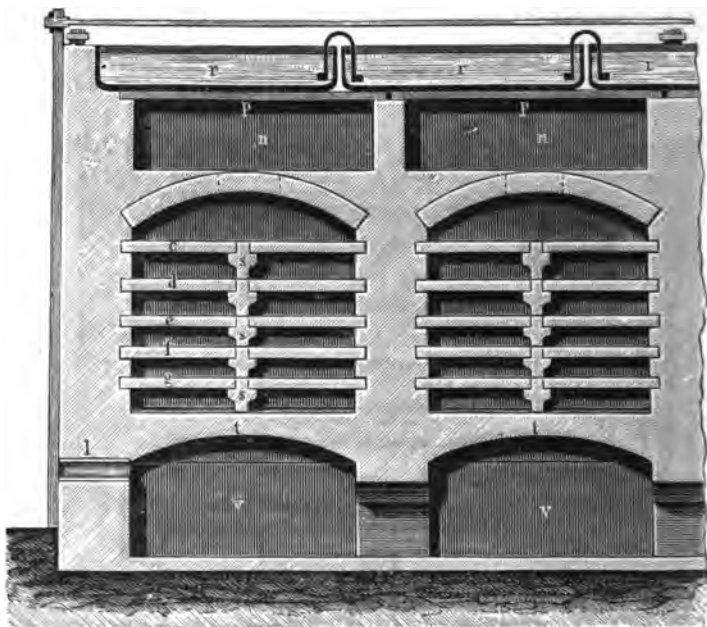
Fig. 60.



During this time the top working-door remains open. Then the five plates *c*, *d*, *e*, *f*, *g* are charged with small ore through the doors *h*, *i*, *k*, whereupon the pyrites takes fire at once. The air enters through *l*, and is regulated at will. The gas travels over all the plates in a serpentine line, indicated by the arrows, escapes through *m* into the dust-chamber, *n*, and through *o* into the acid-chamber or into another dust-chamber. The chamber *n* is covered by a metal plate, *p*, upon which lead pans, *r*, *r*, are placed, in which all the chamber-acid can be concentrated from 112° to 144° Tw. The

acid of one pan communicates with that of another (as usual) by siphons or by simple run-overs. Each of the shelves, which are 8 feet long and 5 feet wide, consists of eight plates in two rows of four each; they rest, at the sides, in the walls of the burner, in the

Fig. 61.



middle on fire-clay bearers, *s, s*, whose shape is better shown in fig. 62. They are not equidistant, as can be seen in the drawing; the upper shelves, where more gas is evolved, are more widely apart than the lower ones, where the radiant heat of the shelves is all the more useful. The best distance for the upper shelves is $4\frac{1}{2}$ inches. In order to burn a larger quantity of pyrites, it is not possible to leave the ore lying quietly, as in Olivier-Perret's burner: since here the external heating by the lump ore is missing, the combustion would be too incomplete, and the heat would soon get so low that the burning would cease. The mass must therefore be moved, which is done in the following way: Every four hours the contents of the lowest plate, *g*, are

Fig. 62.



drawn through the door *k* on to the arch *t* (which is level at the top, but slopes behind), after the burnt ore lying on the same has first been pushed through the same door *k* to the opening into the pit *u*. Then through the door *i* the contents of *f* are pushed down to the plate *g*, and there levelled again. Thus the higher plates are successively treated, till the highest plate, *c*, is emptied and can be charged with fresh ore. If four furnaces go together, one of them is on turn every hour. The contents of the pit *u* are removed once a day by the door *v*. The movement of the ore by removal from one shelf to another causes its thorough combustion, and thus also raises the heat. Four furnaces of the above dimensions burn daily 3 tons of pyrites. From 6½ to 7 lb. of ore are calculated for each superficial foot of shelving.

Sometimes the shelves are made in the shape of a very flat arch, for the sake of greater stability; this is, however, not to be recommended, as the pyrites accumulates in the corners and cannot be got out very well. The top side of the shelves ought to be flat, but the bottom may be arched, especially in the case of wide shelves. Some prefer building the furnaces in such manner that the fire-clay slabs forming the shelves are nowhere enclosed within the brickwork of the walls; they are then more easily replaced when broken.

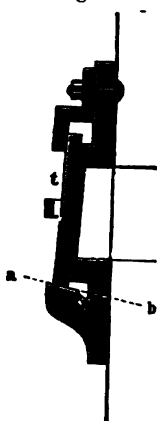
Recently the Malétra burners have been improved by making the fire-clay shelves stronger and doing away with the middle bearers, *s, s* (fig. 62), which give much trouble in working the burner. These single shelves are made from 3 feet 3 inches to 3 feet 7 inches inside.

Malétra's burner, which has obtained general acceptance in Germany, has been improved there by Schaffner, P. W. Hofmann, Bode, and others. Kunheim charges both sides together; so that the time during which the doors are open is much shortened. The burner allows the use of pieces up to $\frac{3}{8}$ of an inch in diameter. Two men per shift usually serve from one to four burners. One man attends upon four of Bode's burners, consuming 3 tons of ore in 24 hours, and at the same time gets out the burnt ore. For wheeling this away one man is occupied for three hours every other shift. Bode's patent circular set of burners professes to be a particularly rational arrangement.

The shelf-burner constructed by Mr. Schaffner, of Aussig, through whose kindness I am enabled to give detailed drawings of

the same, as considered one of the best modifications of this apparatus. It is shown in figs. 63 to 67. It has seven plates, each served through its own door—three on one side, four on the other. On the outside there is also the ash-pit door, 18 inches square, for drawing the cinders, which is thus done in the usual way, not by the rather inaccessible pit of Malétra. The doors all slide with their planed margins on equally planed ledges cast on the front plates; so that luting or plastering is not necessary. A certain number of angle-pieces are bolted to the front plates; these, between their outer bend and the planed ledges, leave sufficient room for the doors to slide each way on the inclined face *a b*; and there is a sufficient number of such pieces present for each door to be always held by three of them (fig. 68). This style of work is evidently much cheaper than casting everything in a piece, because the planing is much easier; it is also cheaper than the English style, shown on p. 231, and quite as substantial as the latter. There are no special openings for the air, as, in spite of the planed surfaces, sufficient air enters to support the combustion. The regulation of the draught is here effected entirely by the chimney-damper.

Fig. 68.



The shelves are made from excellent fire-clay slabs, manufactured at the Aussig works themselves. They are 5 feet long (equal to the width of the burner *plus* the bearing on each side) and 18 inches wide. They run from side to side without any middle bearings, their lower surface being formed in the shape of an arch; so that they are about $3\frac{1}{2}$ inches thick in the middle and 6 inches thick at the ends.

The whole set is covered by a flue dust-chamber, continued into a larger chamber behind, from which the gas during the heating-up goes by an underground flue to the chimney, and during the work itself by a metal pipe to the Glover tower. Through the upper dust-chamber a charging-hopper passes for each burner. The tubular part of the hopper is closed by a small cast-iron cone with its base downwards, which is continued upwards into a rod projecting out of the hopper, and connected with a horizontal lever, whose outer arm has a balance-weight attached to it. By means of this the

hopper filled with small ore can be emptied easily and instantaneously by pressing down the outer arm of the lever. The cone then goes down again, and the joint is made gas-tight by pushing a new charge into the hopper. In this burner *dust and pease* are burnt *together*, and the sulphur burnt down to 1 per cent.; thus the grinding of the smalls, which is still practised at some works, is saved.

One of the principal advantages of the Malétra burners is that the ore is burnt out to a much larger extent not merely than with any of the older forms of dust-burners, but even with the best lamp-burners. Even without grinding the smalls, it is quite easy to keep the sulphur in the cinders down to 1·5 per cent. At many works, *e. g.* at Uetikon, the average amount of sulphur in the cinders never exceeds 1 per cent., and frequently it is below. At Malétra's own works they get down to 0·6 or 0·8 per cent., but this can be done only by crushing the smalls down to an almost uniform fine powder. The amount passed through the burner also influences this. Sorel states that a set of burners, charged with 34 or 35 kils. of ore per square metre every 24 hours, was regularly burnt down to 0·75 per cent.; with 36 kils. the sulphur in the cinders rose to 1 per cent., with 32 kils. it fell as low as 0·42 per cent. Such results can, of course, only be obtained with pure ores, free from zinc, lead, &c. Hence the cinders from shelf-burners are readily bought by iron-works, both for blast-furnaces and other purposes.

In a six-shelf burner there ought to be scarcely any purple flame visible when pulling the charge down from the top shelf to the second shelf. The second shelf is at a bright red heat, the third one less so, and so forth; the back part of fifth ought to be visible only at night by the light radiated downwards from the fourth, and the sixth ought to be perfectly black.

Sorel found the following percentages of sulphur on the different shelves :—

Sulphur in green ore.....	50 per cent.
First shelf	32 "
Second ,,	17 "
Third ,,	7 "
Fourth ,,	5 "
Fifth ,,	2 "
Sixth ,,	0·75 "

He regularly found half of the sulphur in the cinders in the shape of FeS , the other half in that of sulphate.

If there is too much draught, the lower shelves cool down and the upper ones get hotter. This may cause the process to appear as going on very well; but it soon turns out bad. If, on the contrary, there is too little air, the bottom shelf becomes luminous, and the sulphur in the cinders rises rapidly. In both cases there is incipient fusion on the second shelf, which prevents the roasting from being carried through. This can be remedied by admitting a little air at the door of the second shelf, or even mixing a little dead ore with the charge. The admission of air in the intermediate shelves serves also for bringing forward any burners which have got behind, and to burn any sulphur subliming from the first shelf, in case the burners are going too hot, or with damp pyrites giving off sulphuretted hydrogen; but this expedient, useful as it is when properly handled, must be employed with caution lest the bottom shelves get too cold from want of air.

In the normal style of working all the air required for converting the sulphur into sulphuric acid enters at the bottom shelf, and this large quantity of cold air may lower the temperature of the nearly burnt-out mass to such an extent that the ferric sulphate is no more decomposed. It was at first sought at Malétra's works to avoid this by leading the burner-gas downwards underneath the bottom shelf, thus heating this and employing the ground-space as a dust-chamber; but this plan did not answer and was soon given up again. It has even been tried to utilize the heat of the burner-gases for a previous heating of the air serving for the burning-process. But evidently this must most seriously interfere with the draught, and will hardly answer in the long run. The same advantage could be secured more easily by admitting at the bottom only the quantity of air absolutely necessary for completing the roasting of the air, and allowing the remaining air to enter by a regulating-slide in the top working-door. In this case the bottom shelf will be visibly red hot in the dark. This plan can be carried out only where the draught is very good, for instance by making the gas to rise a considerable height before entering the chambers, and never leading it downwards in any part of its course. The burner walls should in this case be made thick to prevent loss of heat in the lower part; on the contrary, an overheating of the top shelf should be avoided by making the gas-flue rather high and causing the heat to be dissipated there, most rationally by means of

evaporating-pans for sulphuric acid. Another plan is, introducing the requisite excess of air into the first chambers by means of an injector.

The Malétra burner answers best for rich ores. With 50 per cent. ore good results are obtained when burning from 32 to 37 kils. of pyrites per superficial metre ($=6.5$ to 7.5 lb. per square foot) in 24 hours. One may go down to 28 kils. ($=5.7$ lb.), but only exceptionally, because the burners cool down too much.

For poor ores, say below 38 per cent. of sulphur, the shelf-burner does not answer.

The management of shelf-burners is really easier than that of lump-burners, but it takes a little more labour. It is generally assumed that one man can charge, burn, and withdraw a ton of pyrites every day; but it is possible to get up to 25 cwt. It seems best to give five burners to each man, so that each burner is charged every five hours. The phenomenon of scarring is hardly ever noticed here. The working-doors must never be left open any more than is absolutely necessary for the work; in this case both the yield of acid and the consumption of nitre are just as favourable when working dust on a shelf-burner as with the best lump-burners. This is the uniform testimony of the many works I have visited.

In order to start a new burner (which, of course, must have been thoroughly dried first in the ordinary manner), the communication with the chambers is stopped, and a fire is lighted on the shelves, beginning with the bottom, sometimes by means of a temporary chimney. After four or five days, when the burner is moderately red hot (it is unnecessary and even injurious to get it up to a *bright* red heat), the remainder of the fuel is cleared away, pyrites is charged on the three top shelves, and communication so made with the chambers, whereupon the regular service is started as previously described.

During the last ten years the shelf-burners have also been introduced into a number of English works, and everywhere with full success. This has been done on the largest scale at the Newcastle Chemical Works (Allhusen's), where 129 shelf-burners on Schaffner's plan described in this book, have been erected, which consume from 600 to 650 tons of pyrites-smalls (Mason and Barry's) per week. Each burner is charged once in 8 hours, with from $4\frac{1}{2}$ to $4\frac{3}{4}$ cwt. of smalls.

Other descriptions of Shelf-burners.

The furnace of Finch and W., J., and S. Willoughby (E. P. 2913, of 1883) differs from a Malétra burner only in that the shelves, instead of being placed horizontally, are inclined alternately in opposite directions.

A modification of the Malétra burner has been patented by Mactear (no. 3701, 1878).

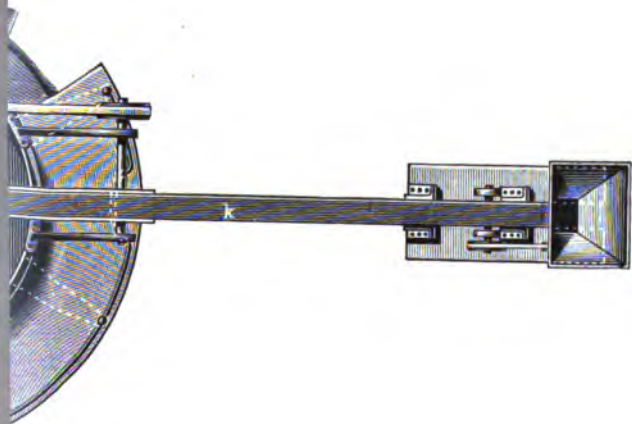
A furnace, combining some of the features of the Gerstenhöfer and the Malétra burners, has been patented by Hasenclever and Helbig (description and diagrams, 1st edition, pp. 220 to 222). It has never been carried out in practice, and is not likely to be so now.

E. Bramwell (G. P. no. 22,758) has constructed a somewhat complicated pyrites-burner, in which, contrary to the ordinary dust-burners, the fresh air meets with the green ore, the products of combustion being gradually led over partially roasted ore, and at last over the almost spent cinders. This is brought about by placing five calcining-beds in a row, each of them provided with an outlet for the gas connected with a gas main, to be connected or disconnected by means of a throttle-valve, so that the current of gases can be directed at will. The last burner of the series communicates with the first by means of a flue underneath, so that a regular rotation can be kept up, as is done in lixiviating vats for black-ash.

The necessity of frequently opening the doors in Malétra's and all similar furnaces is certainly a drawback; it necessitates much labour and cannot but introduce some false air. These drawbacks have been overcome in a most ingenious way in the mechanical pyrites-dust burner constructed by MacDougall Brothers, of Liverpool; but unfortunately new troubles have arisen there which have caused these burners to be abandoned again. Still, as in theory they are the most perfect of all dust-burners, we will give their description here, in the hope that the drawbacks attached to them in their present form may be overcome by future inventions. The MacDougall burner is shown in figs. 69 to 71.

The burner consists of a metal cylinder, 6 feet in diameter and 12 feet high, formed of seven rings (*aa*) bolted together, and provided with a solid bottom, but open at the top. The rings are cast in such a way that the lower and inner edge of each can serve

[To face. p. 260.]



as an abutment for one of the flat arches b_1 to b_6 , which divide the inner space of the cylinder into seven chambers, the uppermost of which is open at the top. The arches, as well as the cast-metal bottom of the cylinder, are pierced in the centre, and allow the passage of a cast-iron shaft, c , 6 inches thick, which is turned by means of the toothed wheel d , the pulley e , and the steam-engine, f . The shaft carries at top and bottom the lutes g and g_1 , into which the cups h and h_1 , fixed to the top arch and the cylinder-bottom, enter; the latter are fast, whilst the lutes g and g_1 turn round with the shaft, and a hydraulic joint prevents the escape of gas at the places where the shaft enters and leaves the cylinder. To the shaft are fixed the cast-iron arms, $i_1, i_2 \dots i_7$, provided with teeth along their lower margin. The teeth are placed alternately in opposite directions; so that the arm i_1 moves the ore-dust from the centre to the periphery, i_2 the same from the periphery to the centre; i_3 acts like i_1 ; i_4 like i_2 , and so forth. Corresponding to this, the arches are perforated alternately— b_1, b_3 , and b_5 near the margin, b_2, b_4 , and b_6 in the centre. The latter have a large central opening, 1 foot 3 inches wide, lined with a metal pipe, which gives free play round the shaft to the gas and the ore-dust; whilst in the other arches the shaft is so tightly surrounded by a metal pipe that scarcely any dust, and still less gas, can get through. The small ore (which need only be passed through a 1-inch riddle, and therefore contains pieces up to the size of a walnut) is lifted by the elevator k (also moved by the engine f), and is emptied on to the top flat, b_1 , where the arm i_1 takes it round and gradually moves it towards the periphery. During this time the ore is completely dried by the heat of the gas below. The ore dropping down the edge at l from the open top chamber is continually pushed into the first closed chamber by a ram at A. The ram A can be moved reciprocally either by the rod B or C, and can be moved more or less quickly; so that the feed of ore can be regulated to a nicety. The arm i_2 moves the ore towards the centre of b_2 , where it drops down; i_3 moves it towards the periphery of b_3 , where it drops down again, and thus quite gradually and constantly, being directed by the teeth of the arms, arrives at the bottom, and is emptied out through the pipe m . The two slides, n and o , allow the contents of m to be got out without any loss of gas or any air entering the other way. As the furnace during the operation is in full heat, most of all near the top, the

ore ignites as soon as it arrives on the bottom of the first closed chamber, b_2 ; and in its gradual zigzag way towards the bottom the sulphur is completely burnt off. The air is continually supplied by the air-pump p in exactly the necessary quantity; and the gas escapes through the pipe r to the acid-chambers.

An apparatus such as is here figured is sufficient for burning $3\frac{1}{2}$ tons of ore in 24 hours; with eight closed chambers instead of six, it can burn 5 tons. It is also very well adapted for burning the spent oxides of gas-works; but then it must have only four chambers. In a factory on the Tyne, where this apparatus was at work for a time, the consumption of coals for driving the engine amounted to 4 tons per week. A two-horse-power engine and a $1\frac{1}{2}$ -inch steam-pipe are said to suffice for the largest burner. The wages amounted to £4 5s. per week; but this rather high amount was explained by the fact that two other furnaces were building, which were expected to be served by the same men who attended the first. Of course this apparatus is quite independent of the skill of the burner-men, which is mostly only acquired by some years' practice.

For heating up, the engine is started and the cold furnace is gradually filled, care being taken to regulate the thickness of the layers of ore on the different floors. When the ore has arrived at the bottom, the engine is stopped, and the flame of a temporary fireplace, built against the cylinder, is allowed to enter it, until the ore lying on the bottom and the floor b_2 has taken fire. Then the engine is started, the temporary fireplace is taken away, the man-hole is closed, and nothing remains but to see that the ore arrives at the bottom properly burnt. If this should not be the case, the speed of the feeding-ram A , that of the air-pump, or that of the agitating-shaft is altered till everything is in order. It is easy to get the sulphur in the burnt ore down to 1 per cent.; in forced work only 3 to 4 per cent. can be attained.

One objection will at once be made to MacDougall's burner, viz. that the machinery in its interior must wear out very quickly. In order to obviate this, all parts of the machinery are made of thick cast-iron; and when one of the arms is worn out, it can be renewed through the man-holes, s, s , without allowing the apparatus to cool down. That otherwise this burner has many very great advantages over all others is evident. The turning of the small ore is perfect without any opening of the doors and working by hand. Not

even during charging and discharging does false air enter the burner; and by means of the air-pump exactly the necessary quantity of air can be admitted (this, however, in practice was found to be very difficult). This work, indeed, is done under such favourable conditions as are realized by no other burner, whether for pieces or for smalls; and it might be assumed that the consumption of nitre would thus be reduced to a minimum, and the yield of acid raised to a maximum. Nevertheless MacDougall's burner had to be given up again in the above-mentioned factory, because the quantity of flue-dust was so great that it could not be managed in any way, and the chamber-process was seriously interfered with. Employment of the Glover tower was not to be thought of. It does not appear that really efficient dust-chambers were employed. The air-pump acted so violently that the dust was carried away a great distance. Probably this drawback might have been counteracted by some alteration in the construction; but, altogether, the machinery caused endless trouble, continually requiring repairs, and there is no doubt that it would have to be altered a good deal before it could become a real success.

A similar furnace was patented by Michel Perret, in France, on June 23rd, 1875. Those who are interested in mechanical calcining furnaces generally will find this subject treated at length by Bode in 'Dingler's Journal,' ccxix. p. 53, and Wagner's 'Jahresbericht,' 1876, p. 298.

The drawbacks objected to MacDougall's furnace are sought to be obviated by a new patent of the same inventor, E. P. no. 3985, of 1883. Dust-chambers are provided with perforated baffle-plates for the interception of dust carried over by the draught, arrangements being made for drawing out the settled dust without allowing gas to escape or air to enter. The shaft and rake-arms are constructed of cast-iron, having a central wrought-iron tube in order to obviate warping or bending from the effect of heat; and in order that the shaft may be readily withdrawn, the arms or rakes are fixed thereto by a fork-shaped end and cotter. A second modification is described, which is to avoid the dust occasioned by the vertical passage from floor to floor. The furnace is constructed of an oblong, horizontal floor or chamber, provided with a series of vertical shafts, having rakes similar to those above described, and revolving in opposite directions. The teeth are so placed as to draw the material towards each shaft, and thus pass it from one to

the other, and from end to end of the furnace. Where prolonged roasting or burning is requisite, a similar furnace, or the first modification, may be superposed above the last mentioned, the material being first passed through the upper furnace.

A mechanical pyrites-kiln, very similar in principle to MacDougall's, has been patented by R. Mackenzie (E. P. no. 4418, 1881). It is provided with a water-cistern at the bottom, in the hope of promoting the process by the presence of aqueous vapour.

Another similar furnace, differing only in details of construction, has been patented by Black & Larkin (E. P. 4456, of 1881).

Farmer and Hardwicke's mechanical pyrites-burner (1878) resembles to some extent Jones' and Walsh's mechanical salt-cake furnace. It is automatically charged and emptied; $5\frac{1}{2}$ tons of pyrites are said to be burnt off in from 7 to 9 hours. None of these furnaces seem to be in practical operation.

The mechanical pyrites-burner of P. Spence (patented in England Dec. 24, 1878; in Germany No. 9267; in America No. 248,521) is a shelf-burner, provided with mechanical stirring arrangement. As this furnace seems to be constructed on rational principles, and as it has met with practical success in America, we give here a complete description of it.

Fig. 72 shows an exterior side view; fig. 73 a plan; fig. 74 a cross section of one half of a double furnace, the other half being shown in outside view; fig. 75 a longitudinal section of the furnace-beds; and figs. 76, 77, and 78 views of the stirring and raking instruments. The construction of the furnace-beds is best seen from fig. 74. In this there are at 1 the walls of the furnace, in which are fixed projecting fire-clay slabs, 2. Upon these are placed tiles, 3, reaching from one side of the furnace to the other, a number of these composing the length of each furnace-bed. In figs. 74 and 75 the several beds are shown at 3, 3a, 3b, 3c; alternate openings in these beds being shown at 4, 5, 6, 7. The pulverulent material is thrown at H on to the floor 3; advancing rakes or ploughs stir it and carry forward a portion of it through the opening 4 on to the second bed 3a. The teeth of the rakes are formed of a triangular section, as shown in fig. 78, the apex of the triangle being in the direction of the motion of each rake longitudinally from end to end of the furnace, the flat sides of the teeth of the rake being in the direction in which it is desired to traverse the ore along the bed of the furnace. When the rake is advancing in

Fig. 72.

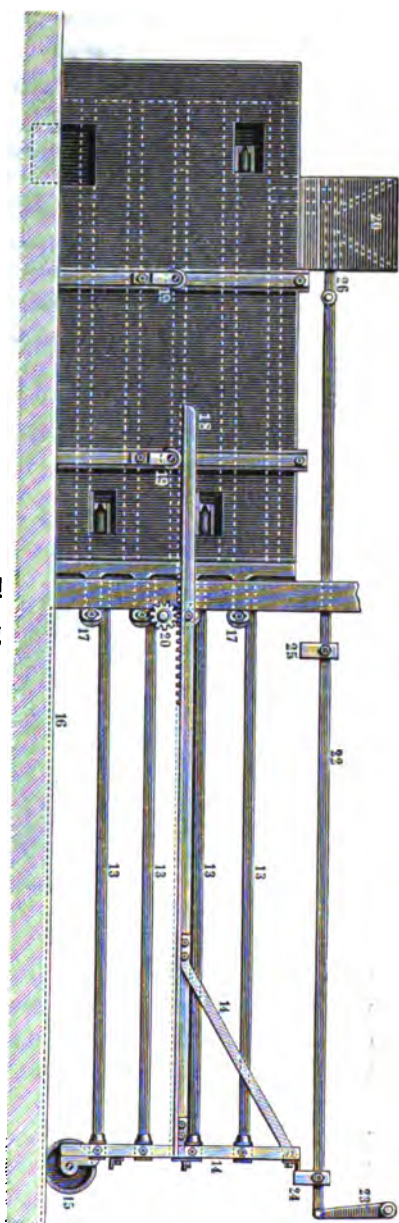


Fig. 73.

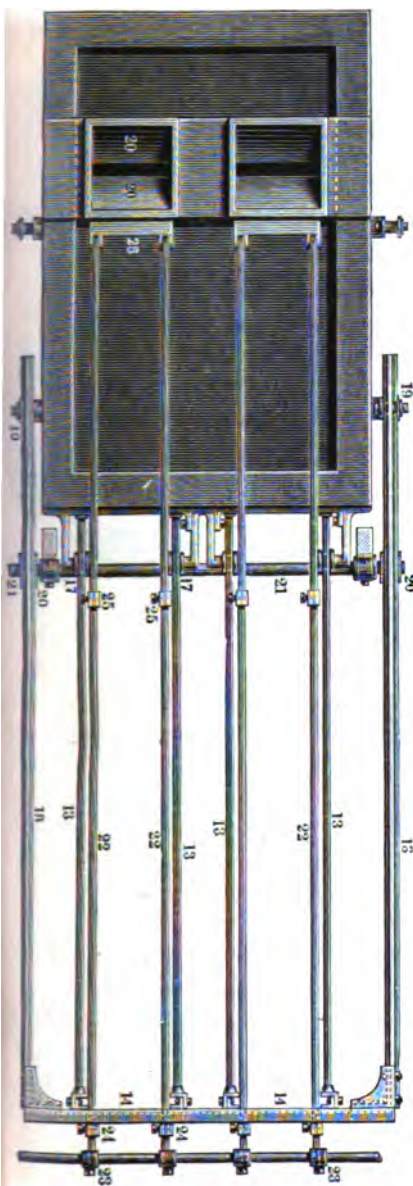


Fig. 75.

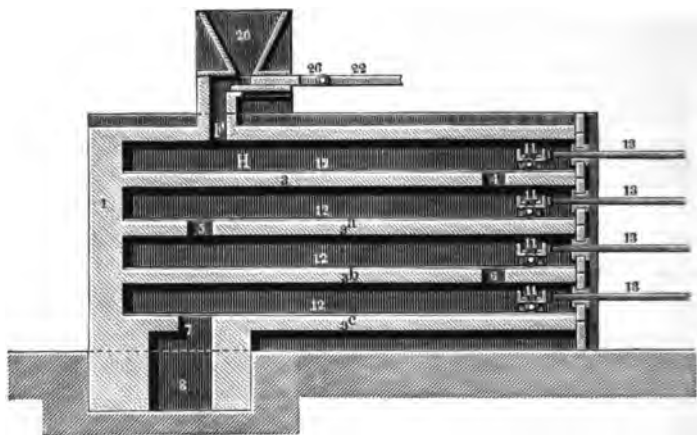


Fig. 74.

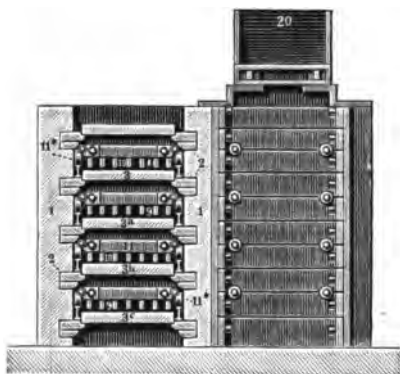


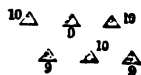
Fig. 76.



Fig. 77.



Fig. 78.



the direction of the pointed part of the teeth of the rake, the ore will be turned over only; but when the rake is moving in an opposite direction, a certain quantity of the ore will be carried by the flat side of the teeth along the floor of the furnace. Thus the ground material, delivered to the floor 3 at the point H, is stirred and subsequently partially carried forward till it is delivered through opening 4 on to the second bed, 3a, where the same operations take place, the material now passing down the opening 5 on to the bed 3b, and so through all the beds, until it is at last

discharged through the opening 7 into the receptacle 8. Since the openings in the successive beds are on alternate ends of the furnace, the stirring and conveying instruments must be reversed as regards their faces in succeeding beds. The teeth of the rakes are mounted in angle-iron bars, 11, provided with rollers, 11*x*, which run upon rails, 12, carried by the projecting supports 2. To each of these angle-bars are connected rods, 13, attached at their other ends to a frame or carriage, 14, provided with wheels, 15, which run upon rails, 16, on the floor, the said rods being supported and guided by grooved pulleys, 17. On the carriage, 14, are fixed toothed racks, 18, situated outside the furnace, and supported at their outward ends by rollers, 19, and in gear with these rods are pinions, 20, on a shaft, 21, driven by motive power. Motion being communicated to the shaft, 21, the pinions, 20, cause the racks, 18, to traverse the frame, 14, which, as stated, travels on the rails, 16, and thus the rods, 13, are caused to traverse the rakes or conveyers along the several beds of the furnace. According to the positions shown in the drawings, the carriage 14 is in its outward, or nearly outward, position, and the flat ends of the instruments will have delivered a certain amount of material through the opening 4 on to the bed 3*a*, the same operation having taken place with regard to the opening 6 and bed 3*c*. The carriage now running inward, the sharp points of the ploughs will simply stir the material on the beds 3, 3*b*, while the blunt ends on the floor 3*a* will deliver a certain quantity of material through the opening 5 on to the bed 3*b*, and at the same time the instruments on the floor 3*c* will pass an amount of completely calcined material into the receptacle 8, to be removed at pleasure. The feeding of the furnace takes place in the following manner:—At F is a channel leading to the top floor 3, and above this channel is a hopper, 20, into which the ground material is from time to time fed. The bottom of this hopper is provided with a sliding plate, 26, formed at its inward end with a ledge, as seen in fig. 75. This plate is connected to rods, 22, swung upon arms, 23, and each having two stops, 24, 25. According to the position shown, the material rests upon the ledge of the plate, 26, which, when the carriage runs in, is pushed forward by its arrival in contact with the stops 24, and this action delivers a certain amount of material through the channel F. On the return motion of the carriage the stops 25 shift the plate 26 back, and so on. Instead of plate 26, there may be a winged bottom to the

hopper. The furnace may be single or double, the latter (which is shown in the drawings) being preferred. The shaft 21 is connected by means of suitable gearing to any source of motive power, so that it may be rotated first in one direction and then in the other, and thereby traverse the rakes alternately from one end of the furnace to the other. The rakes may move continuously; but it is preferable that they should remain stationary periodically in the position shown in the drawings, as they are then clear of the ore and out of the direct action of the heat, thereby suffering less injury from corrosion.

A number of these furnaces have been put up by the Sulphur Mines Company of Virginia, at Baltimore. According to a communication, kindly made to me in May 1888 by the President, Mr. Crenshaw, three double furnaces are connected with a set of chambers of 180,000 cubic feet capacity, with Glover and Gay-Lussac towers, two other furnaces to a set of 126,000 feet. The 5 furnaces were to burn 14 tons of 47/48 per cent. pyrites each 24 hours, down to less than 2 per cent. of sulphur in the cinders.

Spence's furnace conveys the impression of being a more durable piece of work than the more ingeniously elaborated furnaces above described. The furnace itself is as easily constructed as an ordinary shelf-burner, and the movable parts are nothing like so much exposed to the action of the fire and the acid gases as in MacDougall's furnace. It is also probably easier to keep the flue-dust within reasonable limits. The advantage in comparison with an ordinary shelf-burner is both in the saving of labour and in doing away with the necessity of constantly opening the working-doors. Thus Spence's furnace seems certainly a step in the right direction; but no doubt prolonged experience only can decide whether it will ultimately effect its purpose or not.

It is mentioned as a drawback of Spence's furnaces that at the back end a collection of dust takes place by which the rakes are prevented from doing their work properly. Bartsch, of Bridgeport (Fischer's *Jahresb.* 1886, p. 256), consequently applies to the furnace ends a separate set of broad plates, moved by a second moving-frame in such way that the dust is cleared out automatically every time the principal frame is made to work.

The ordinary shelf-burner has been combined with a mechanical arrangement by Hering (G. P. 9634), who feeds the top shelf continuously by means of a screen, the burnt ore being removed from the bottom shelf by another screw.

T. Mason (E. P. 3196, 1880), employs a furnace with a bed

slanting slightly downwards, across which there are lying a number of fluted rollers (say 20), made of cast-iron or stoneware, moved by means of gearing outside the furnace. The pyrites-dust is fed mechanically into a hopper, situated at the upper end, and is gradually moved down the inclined hearth by means of the fluted rollers, the cinders being discharged at the lower end. A furnace placed below gives additional heat in the case of poor ores. (It is not likely that such an arrangement would stand the wear and tear unavoidable in this case.) Modifications of this furnace are contained in the patent No. 1788, of 1881, and No. 2831, 1882.

Walker and Carter (E. P. 4000, 1883) employ for roasting pyrites a set of eight horizontal cylindrical retorts (four tiers of two each), heated outside by an ordinary coal fire, and communicating by openings at alternate ends. Hollow shafts, provided with stirrers, pass through each retort; cooling-water runs through all these shafts from one to another and prevents their warping. Special contrivances prevent the stirrers from touching the sides of the retorts in spite of unequal heating. The broken ore is fed into the top retorts and gradually finds its way into the three following tiers; a current of air traverses the retorts in the opposite direction. This apparatus is stated to have worked well for roasting pyrites containing 42.2 per cent. sulphur (Engineering and Mining Journal, xxxvii. p. 294), but it does not convey the impression that it would go on for a long time without very heavy wear and tear; and the necessity of an outside fire also militates against it. The report made on this burner by W. Martyn (J. Soc. Chem. Ind. 1885, p. 26) is not encouraging.

W. Brückner (Engineering and Mining Journal, xxxvii. p. 425; Fischer's Jahresb. 1884, p. 221) employs for roasting pyrites-smalls the principle of a horizontal cylindrical revolving furnace. As this furnace is provided with internal firing, and the SO_2 gets mixed with all the smoke-gases, it is hardly intended and certainly not adapted for serving in the manufacture of sulphuric acid. This is, on the contrary, the aim of an apparatus patented by R. and C. Oxland (E. P. No. 7285, 1885), who roast the pyrites in a revolving cylinder of 30 feet length heated from the outside, so that the SO_2 is kept apart from the smoke-gases. At the lower end of the rotating tube is a cast-iron prolongation, heated externally by a fire-grate and flues. The amount of air admitted to the calciner is regulated by a contrivance in the end plate of the prolongation, which is also fitted with a door for the removal of the

cinders. (This apparatus seems to be more intended for roasting arsenical ores, and recovering the white arsenic in the process.)

K. Walter has constructed a special burner for "*peas*," that is, small pieces of ore between the size of a hazel-nut and such as pass through a sieve with eight holes to the lineal inch. This apparatus is described and figured in the 1st edition, pp. 225 to 229. It has grate-bars laid sideways across the burner, cast with projections beneath, through which a bar passes. This makes it possible to turn all the bars at the same time and exactly in the same way. The spaces between the bars can therefore be made very small, so that the "*peas*" do not fall through without the bars being moved; and as they lie only 6 inches thick, the air can pass through with the ordinary draught. Each compartment, with a grate surface of 32 square feet, burns from 14 to 20 cwt. in 24 hours.

Walter's burners require a strong draught, and must be worked for a separate set of chambers; with insufficient draught very large scars are formed at once. As they are only adapted for a special size of ore, they have not met with any extended application.

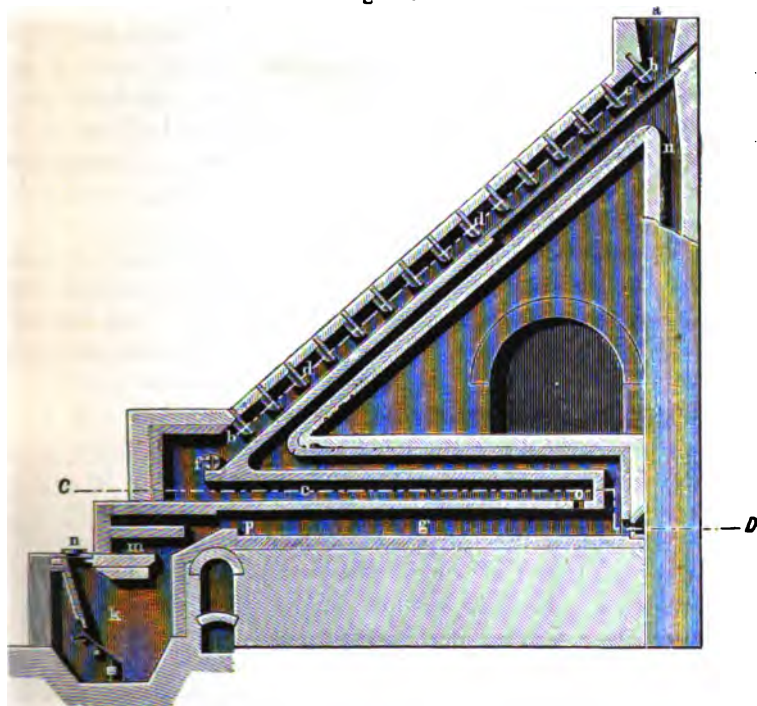
4. BURNERS FOR ZINC-BLENDE.

Zinc-blende is now the most important of all zinc-ores, and all of it must be converted into zinc oxide by a thorough roasting. This is nothing like so easy as with pyrites, as, on the one hand, blende contains at best only about 35 per cent., often only 20 per cent., of sulphur, and, on the other hand, it is much more difficult to burn out than iron or copper pyrites, zinc sulphate being formed and being very difficult to decompose. As the manufacture of zinc requires nearly all the sulphur to be driven off, and as the burners employed for pyrites are useless in the case of blende, the latter was formerly roasted in reverberatory furnaces, all the sulphurous acid passing away with the furnace-gases. This would probably be done even now, if the damage caused by the acid smoke had not caused the sanitary authorities, both in England and on the Continent, to impose upon the manufacturers the duty of doing their best to condense the acids contained in the smoke, the damage caused by which has been described *suprà*, pp. 101 *et seq.*

The development of the processes for abolishing the acid-smoke nuisance and utilizing the sulphur in connection with the roast-

ing of blende, at least in one of the most industrial parts of Germany, has been described at length by Hasenclever (*Zeitschr. des Vereins deutsch. Ingenieure*, 1886, p. 83; *Fischer's Jahresh.* 1886, p. 257), of whose paper we give a short abstract. Before 1855 all the blende consumed at the large Stolberg zinc-works was roasted in ordinary open furnaces by a direct coal-fire, the

Fig. 79.



gases from which contained only about 0.75 per cent. SO_2 by volume and escaped into the atmosphere. In 1855 the Rhenania chemical works at Stolberg erected a furnace, intended to utilize the larger portion of the SO_2 . It consisted of a long muffle-furnace in which the ore was shifted along the hearth from back to front by manual labour (evidently identical in principle with Spence's first furnace, *suprà*, p. 248). Thus half the sulphur could be utilized for the manufacture of sulphuric acid, but with great waste of nitre. Godin improved this furnace by placing a series of muffles on the top, which the ore had to pass gradatim; but this apparatus was given up again for the Gerstenhöfer furnace

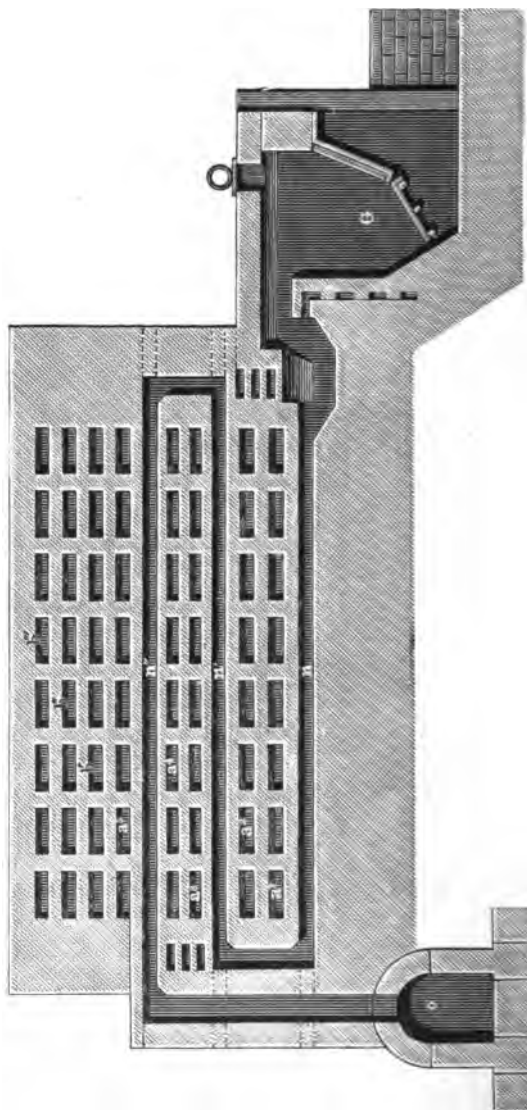
(*suprà*, p. 250). By this comparatively rich gases were obtained, but the immense quantity of flue-dust was very troublesome, and it proved too difficult to combine this furnace with another for finishing the roasting. After this several constructions were tried by Hasenclever and Helbig, but these showed various drawbacks; and this led in 1874 to the construction of a new furnace, which has been at work for a number of years, not merely at Stolberg, but at many other German works. This new Hasenclever furnace has been described and illustrated in the first edition of this work, pp. 201 to 204; we describe it briefly here. It consisted in a reverberatory furnace, *g*, on the top of which was placed a muffle, *c*, reaching all over its length. The bottom of this muffle, fig. 79, forming the top of the reverberatory furnace, was heated directly; the flame of the furnace, passing over the roof over the muffle, heated this as well, and then passed under an inclined plane at an angle of 43° , at the top of which, at *a*, the fresh (powdered) blende was fed in. The ore, on sliding down that plane (partitions, *d, d*, preventing its transit from becoming too rapid), underwent a preliminary heating by the hot gases passing underneath; this heating was continued in the muffle *c c*, where air was admitted and as much of the sulphur was burned away as possible. At last the semi-burnt ore was pushed down into the furnace *g*, where it was burned completely by the fire from the gas-producer *k*. The sulphur dioxide formed here is certainly lost, and it formed no inconsiderable portion (generally more than one third) of the whole; but that formed in the muffle and on the inclined plane is strong enough to be carried into lead-chambers and converted into sulphuric acid, certainly at no great profit, if any. A large number of Hasenclever furnaces were erected on the Rhine and in Silesia, but they were found to utilize on an average only 60 per cent. of the sulphur as sulphuric acid. The remaining 40 per cent. SO_2 , being mixed with the fire-gases, still escaped into the atmosphere and were blamed for even more damage than they actually caused, the part taken by the numerous zinc-works, glass-works, &c. being generally overlooked by the public (comp. p. 105). In order to deal with the SO_2 contained in the smoke-gases, many processes were tried at Stolberg on a large scale (described at length by Hasenclever, Fischer's Jahresb. 1881, p. 173). Absorbing the SO_2 by milk of lime is only practicable for small quantities; at Stolberg, where the different works emit daily over 80 tons of SO_2 into the atmosphere, it would be

much too costly. Absorbing by water in a large leaden coke-tower was not at all efficient (compare, however, *infra*, the process of Schroeder and Haenisch). A thorough trial was made of the proposal of Freytag (G. P. 14928 and 15547), absorbing the gases by sulphuric acid of spec. grav. 1.53, which retains both SO_2 and SO_3 , and arrives at the bottom 1.634 to 1.671 strong. But this process leaves no profit; there is still some SO_2 in the exit gases which must be absorbed by milk of lime, &c. Attempts at producing in this way bisulphite of lime as a commercial product were not successful. A process patented by A. Winkler (G. P. 14425) was also tried; it consists in absorbing the SO_2 by scrap iron, kept moist by a stream of water; this was evidently too dear. Even the use of limestone or dolomite (*vide infra*), with the attending labour, costs a good deal; and it is even worse that *all* the just-mentioned, or any other absorption processes, involve very troublesome preparatory operations, such as producing considerable draught, keeping out the flue-dust, cooling the gases, &c. Recently a number of blende-roasting furnaces have been constructed which permit of utilizing the whole of the sulphur of the ore in vitriol chambers, and thus do away with the extremely troublesome processes for absorbing SO_2 from fire-gases. All these modern furnaces have one principle in common: they combine the heat produced by the burning of the blende sulphur with heat applied externally, but in such manner that the fire-gases are kept entirely separate from the roasting-gases. It has been found that this indirect heat suffices for completely roasting the blende.

The furnaces which first realized the principle of utilizing all the sulphur of the blende in vitriol-making, by completing the roasting by means of indirect fire, were invented by M. Liebig, who had the idea of constructing a sort of shelf-burner with shelves, partially hollow, and heated by indirect fire. His invention (G. P. 21032 of Eichhorn and Liebig) is shown in figs. 80 and 81. Liebig's furnaces consist of a number (say, seven) of separate burners, as shown in fig. 80, each of them consisting of 5 heated shelves, a^1 , a^2 , a^3 , a^4 , a^5 , and three unheated shelves, b' , b'' , b''' , all of them being accessible either on one side or on the other through the working doors, c , c . The heating is performed by the flame issuing from the gas-producer G , and travelling in the flues n , n , along the whole length of the seven burners, returning towards the front end in the higher flues n' , n' , and again in the top flues n'' , n'' , in order to leave by the main flue o . The air

required for roasting the blende enters through door *d*; it is exposed to the heat radiated from above by flue *n*, by traversing the flue *e*, before it reaches the bottom bed *a*¹. The blende,

Fig. 80.

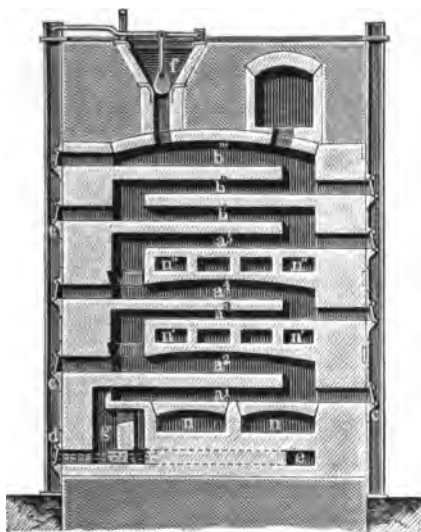


warmed up on the top of the burners, is charged through hopper *f* on to the top bed *b*^{'''}, where it takes fire, and after six or eight

hours is gradually shifted down b'' and b' to a^s . Here, where its own heat of combustion is already low, it receives the heat of the top flue, and on gradually descending down to a^1 it meets hotter and hotter shelves, so that at a^1 its roasting is complete, aided by the above-described heating of the air in channel e . The cinders are pushed over into pit g , from which they are withdrawn. Altogether the ore remains about 48 hours in the burner. In a special experiment the fresh ore contained 27·8 per cent. sulphur; after six hours' stay on the top shelf it contained 24·9 per cent., on the following four shelves 17·3, 13·2, 2·3, and 0·2, at the bottom only 0·1 per cent. sulphur. The burner-gases contained 5 or 6 per cent. SO_2 .

Eichhorn states (Fischer's Jahresb. 1889, p. 322) that a

Fig. 81.



furnace of the kind just described furnishes within 24 hours from 4·2 to 4·5 tons of roasted ore, with 4 men's labour (2 in each shift) and 16 cwt. of coals. The sulphur of the blende itself left in the product is only 0·1 per cent., but in the presence of carbonate of lime of course a corresponding quantity of sulphate is formed. The gases contained 6 to 8 per cent. SO_2 , against 2 per cent. from Freiberg kilns.

Michel Perret (G. P. 37842) has modified his well-known furnace for burning fuel in the shape of dust so as to roast blende,

without mixing the fire-gases with the gases evolved by the burning blende. The principle is very similar to that of Eichhorn and Liebig. So are the furnaces described by Hasenclever in Fischer's *Jahresb.* 1886, p. 260, and those patented by Grillo (G. P. 28458).

Mechanical blende-burners are the following:—The burner patented by J. Haas (G. P. 23080) is very similar to MacDougall's (comp. p. 260), but the single chambers, in lieu of having simple brick bottoms, are separated by flues through which pass the fire-gases from a coal-fire. Mechanical stirrers move the ore from the top shelf over three others and ultimately into an open hearth, where the last roasting takes place.

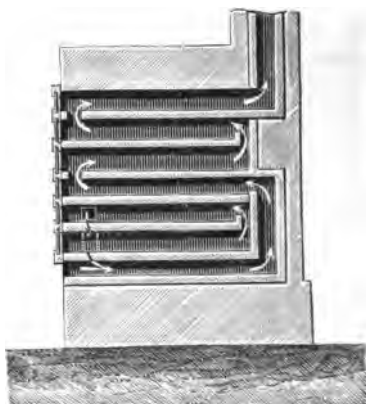
Hegeler's burner is a combination of an Eichhorn and Liebig's burner with a stirring arrangement somewhat similar to Spence's (p. 264), but differing from it in some important practical details. This furnace works most successfully at Mathiesen and Hegeler's zinc-works, La Salle, Ill.

The burners patented by the Société Vieille Montagne (G. P. 24155 and 36609) are mechanical burners in which the flame of the coal-fire is not separated from the roasting-gases.

5. BURNERS FOR THE SPENT OXIDE OF GAS-WORKS.

The spent oxide is now generally washed, so as to obtain ammonia salts therefrom, and is also frequently treated for the ferro-

Fig. 82.



cyanide or sulphocyanide. At all events the sulphur, which it contains in the free state, sometimes up to 50 per cent., is ulti-

mately burnt for the manufacture of sulphuric acid. This is sometimes done in ordinary brimstone-burners, as shown *suprà*, p. 194 *et seq.*; but in this case it is difficult to burn it out completely, and there is loss of sulphur in the cinders. Ordinarily it is burnt in apparatus very similar to "shelf-burners," as shown in fig. 82 (Hill's burner). Each chamber in this case is about 10 feet long, 20 inches wide, and 9 inches high. MacDougall's mechanical burner (p. 260) has also been employed for this purpose.

Cowen's burner, figs. 83 and 84, consists of a row of fire-clay gas-retorts, and requires no further explanation. Other works are said to burn that material in burners with very narrowly-placed grate-bars.

Fig. 83.

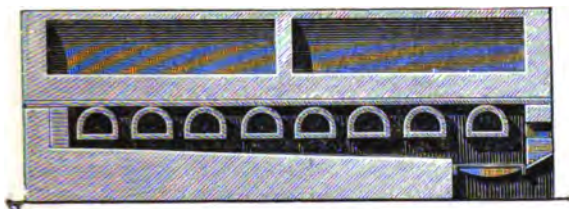
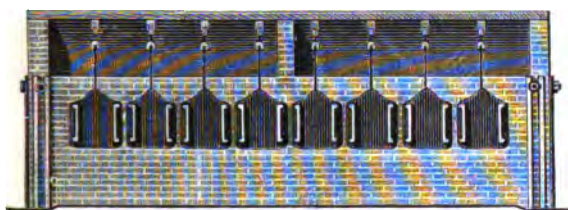


Fig. 84.



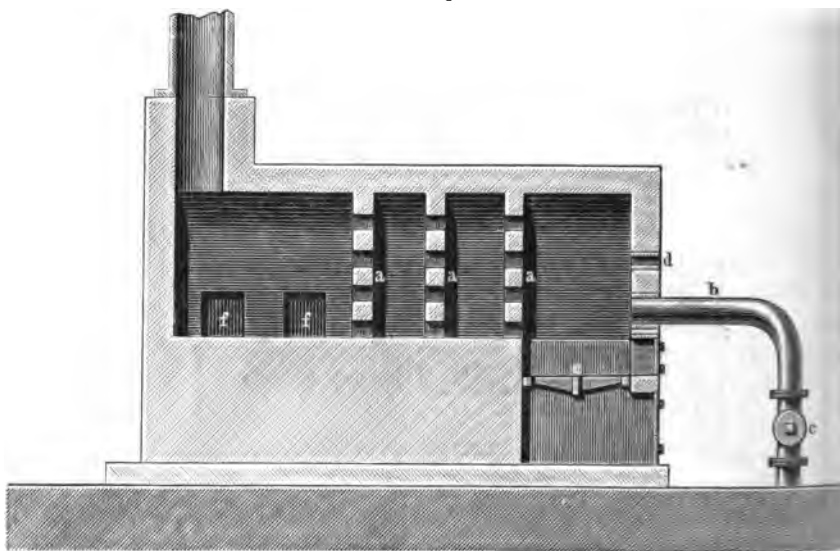
Sometimes the oxide is moulded into bricks and put into lump-burners; it burns off very well and the cinders fall through the grate-bars by themselves; in fact, the bars must be touched as little as possible. This process does not answer so well as shelf-burners.

6. BURNERS FOR SULPHURETTED HYDROGEN.

These are usually of a very simple description. As shown in fig. 85, they consist of a brick-chamber provided with some baffling-

walls *a, a*. The sulphuretted hydrogen gas (which is nearly always mixed with a large quantity of inert gas, chiefly nitrogen) is introduced by the cast-iron pipe *b*, the supply being regulated by an inlet-valve *c*. Air is admitted partly round the pipe *b*, partly by a special opening *d*, which ought to be provided with a slide or other means of regulating the amount of air. The heat produced by the combustion of the sulphuretted hydrogen is quite sufficient for keeping the temperature of the chamber at a red heat, so that the gas is always lighted again if by chance the flame has been extinguished. This is aided by the baffling-walls *a a*, which serve both the purpose of supplying a reservoir of heat for the just-mentioned purpose, and of mixing the gases so as to insure perfect combustion. The grate, *e*, is required only for irregularly composed gases, like those formed in the saturation of the gas from ammonia-stills

Fig. 85.



by sulphuric acid; especially for re-lighting the gas after stoppages over Sundays, and so forth. With gases of regular composition and comparatively rich in sulphuretted hydrogen, like those given off in Chance's sulphur-recovering process, the grate *e* is quite unnecessary, as these gases are as easily lighted and kept burning

as coal-gas. The doors *ff* serve for "potting" the nitre, where it is not preferred to employ more rationally constructed apparatus for this purpose (comp. Chapter VI.). The size of the whole chamber may be about 10 to 12 feet long, 4 or 5 feet wide, and 3 feet high. Pans for concentrating sulphuric acid may be placed upon it, and even in this case the gases will issue hot enough to do full work in a Glover tower. Sublimation of sulphur is never observed with ordinary care in admitting the air. One very great advantage in burning sulphuretted hydrogen is this: that, contrary to the variations in the amount of SO_2 in burning brimstone or pyrites, even when keeping up a regular rotation of the burners, there is in this case a perfectly continuous process, as the supply of H_2S from the gas-holder is continuous; the amount of air need never be varied when once regulated; the percentage of SO_2 in the burner-gas is altogether uniform; the chamber process is consequently much more regular than with brimstone or pyrites, and the consumption of nitre is correspondingly smaller. All this, however, holds good only if the percentage of H_2S in the gas is practically constant, whilst with gases of very varying composition, like those evolved in ammonia works, the very contrary is the case.

It must be remarked that at some works, in burning the sulphuretted hydrogen from the Chance process, an increased consumption of nitre has been noticed, whilst at others a saving in nitre in comparison with the burning of pyrites has been effected. Evidently in the former case the quality of the sulphuretted hydrogen has not been as it ought to be; it has no doubt varied in percentage, and may even have contained a notable quantity of carbonic acid, so that the chamber-process would not be as regular as desirable. Sometimes it has been noticed that the combustion has not been quite perfect, so that sublimed sulphur has been found in the Glover tower or even in the chambers; but this is evidently owing to mistakes and careless work, and should not occur with ordinary care.

In 1886 E. Lombard (Monit. Scient. 1889, p. 1231) described a shelf-burner for sulphuretted hydrogen, consisting of two separate compartments, 7 ft. 6 in. deep inside. There are four shelves, 6 ft. 6 in. long and 1 ft. 4 in. wide, formed of four fire-clay slabs each. The top shelf is perforated with many holes, and occupies the whole length and width of the furnace; the other shelves are not perforated, and leave at alternate ends a passage of 12×16 in.

for the gases. Each furnace is provided at the base with four burners for H_2S and two air-tubes, disposed in two tiers of three each, the air-tubes occupying the central places. The burners consist of fire-clay tubes, 6 ft. 6 in. long, $1\frac{1}{2}$ in. wide inside, and $\frac{3}{8}$ in. thick, projecting two-thirds of their length into the furnace, and provided on the top with slits or holes for dividing the gas. They are connected in front by a cast-iron tube with stop-cock for regulating the flow. The air-tube is $2\frac{1}{2}$ in. wide, and is provided with an iron thimble for regulating the quantity entering. The gaseous products of combustion pass into a flue, 1 ft. 6 in. \times 2 ft., on the top of the furnace, then into a small dust-chamber, and then into the Glover tower. Total height 6 feet. The pressure of the gas is $= 1\frac{1}{2}$ inches of water; it is said to work very well.

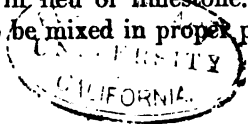
Simpson and Parnell (E. P. 14711, 1886) regulate the supply of air and gas in any desired proportion, so as to obtain either free S or SO_2 , by employing two vessels, each of which is provided with an inlet and an outlet valve. Both vessels are filled and emptied simultaneously by a mechanical arrangement, the two vessels acting in conjunction, so that the gas entering and leaving one of the vessels bears a constant proportion to the quantity of air entering and leaving the other vessel. [Such an arrangement, very useful as it undoubtedly is for the production of free sulphur from H_2S , seems unnecessarily complicated when the object is that of burning the H_2S with an excess of air for the purpose of sulphuric-acid manufacture.]

7. PROCESSES FOR ABSORBING SULPHUROUS ACID CONTAINED IN ACID-SMOKE, FIRE-GASES, AND THE LIKE.

The abatement of the nuisance caused by the acid-smoke given off in metallurgical and other operations presents special difficulties where the percentage of acids is so slight that their utilization by condensation or by conversion into sulphuric acid is out of the question; that is, if less than 4 per cent. SO_2 by volume is present. We have already, in connection with the roasting of blende (p. 271 *et seq.*), mentioned several of the processes intended to remove the sulphur dioxide and other acids from smoke-gases: they all have as a common feature that they are very expensive, and that at the same time they hardly ever attain their purpose completely. The problem of dealing with the enormous quantity of SO_2 contained in ordinary coal-smoke has been hardly ever attacked in a serious

manner, as the expense and inconvenience of any imaginable measures for this purpose have hitherto appeared to be quite unbearable; and it does not seem as if this would be different in a near future. The only practicable remedy in this case, as well as in some cases of metallurgical smoke, is diluting the gases with a large quantity of air, by erecting very tall chimneys for carrying them up to a considerable height above the surface of the earth. Such chimneys have been made up to 450 feet in height. In the case of hydrochloric acid they have entirely failed in their object, as we shall see when treating of the condensation of that acid in the manufacture of sulphate of soda, but in that of sulphurous acid the dilution of air is more efficient. Freytag certainly estimates (somewhat arbitrarily) that smoke is harmless only when it does not contain beyond 0.003 per cent. SO_2 by volume; but as, for instance, in lead-works the percentage of SO_2 in the main flues, where all the smoke and fire-gases are mixed, rarely exceeds 0.1 per cent., it is very likely that, if these gases are allowed to escape only 200 feet or more above any vegetation, they get sufficiently diluted with air in their descent to become harmless. This is owing to the fact that sulphur dioxide diffuses pretty equally in the air, whilst hydrochloric acid, sulphuric anhydride, acid salts, &c., which form visible fumes, generally reach the bottom in a very little divided stream, and cannot therefore be made innocuous by very tall chimney-shafts. In fact, this is the only explanation why the scores of tons of SO_2 daily belched forth in certain localities by lead-works, zinc-works, glass-works, &c., have not ere now destroyed all vegetable life around the works, which is notoriously the case only in a few isolated instances. But as such instances do occur, and as altogether the requirements of sanitary authorities are constantly becoming stricter, the removal of the acid-smoke to a high level by means of chimneys cannot be pronounced a final solution of the difficulty, even where only SO_2 is the acid concerned, all the more as in moist weather the acids escaping from the very tallest chimneys are brought down to the ground in a somewhat concentrated state.

O. Schott (Dingl. Journ. ccxxi. p. 142) has proposed to utilize, for citriol-making, the sulphurous acid given off in making glass from sodium sulphate. The gas is to be made richer in sulphur by employing for the glass-mixture gypsum in lieu of limestone. Sulphate of soda, gypsum, and coal are to be mixed in proper propor-



tions, and brought to a bright red heat in muffle-furnaces or in elliptical glass pots, until the SO_2 is driven off. The fritted residue of sodium and calcium silicate is to be powdered and used by glass-works; the gas is to be conducted into lead-chambers and worked for vitriol. This process seems entirely impracticable; especially since such diluted gas (mixed with a great deal of carbonic acid) has not yet been utilized.

Thirion (Fr. P. Feb. 28, 1874; Wagner's Jahresb. 1875, p. 391) makes a similar proposal for heating sodium sulphate with coal and silica, whereby a mixture of sulphur vapour, sulphur dioxide, and carbon monoxide is cooled. The sodium silicate is to be decomposed by CO_2 or to be used as such. [As a proposal for manufacturing sulphur or sulphuric acid this process is evidently hopeless.]

We will now give a synopsis of the various methods for treating acid-smoke, with special reference to the removal of SO_2 and SO_3 . For details we must refer to the sources quoted in the text and to a special treatise by C. A. Hering, "Die Verdichtung des Hütten-rauches" (Stuttgart, 1888).

Condensing by water seems to be the simplest and most obvious process, looking at the great solubility of sulphurous and sulphuric acid in water. But this process is in reality only practicable where the percentage of acids is not too slight; dilute acid smoke is not sufficiently washed without employing a comparatively enormous quantity of water; and, surprising as it is, SO_3 is even more difficult to condense in this way than SO_2 . It is quite certain that condensation by water can be made to *pay* only where the gases are sufficiently concentrated to convert them into sulphuric acid in lead-chambers; it is therefore the interest of smelting-works, &c., to conduct their processes in such manner that the acids are diluted with as little inert gases as possible. If the percentage of SO_2 reaches 4 per cent. by volume, they may be submitted to the Schroeder and Haenisch process (*vide infra*), or they may even be converted into sulphuric acid, although this will hardly leave much profit at that percentage; but it is enough to have removed the nuisance. Where, however, there is less than 4 per cent. of SO_2 in the gases, any *utilization* is out of the question; the thin acid liquids obtained by washing the smoke must be run to waste (which in most cases means a fresh nuisance, and is not permitted by the authorities); nor is the SO_2 and SO_3 anything like completely

taken out of the gases; and the nuisance is at best only diminished, but not remedied.

At all events the contact of the absorbing-water with the acid gases must be made as intimate as possible. The condensing-apparatus used for hydrochloric acid, and described in their place, act only for somewhat strong gases; the weak gases which we are here treating of require special means, such as paddle-wheels or similar spray-producing apparatus, costly to work and to keep in repair, and generally imperfect in their action.

In lieu of water, Freytag (G. P. 9969, 14928, 15546) and Hasenclever (G. P. 17371) employ somewhat concentrated *sulphuric acid*, in an ordinary coke-tower of large size. This agent retains the SO_2 much better than water, so that in some cases the expense of working the process is paid by the sulphuric acid gained (comp. *suprà*, p. 273). SO_2 is also retained to some extent, but only if the gases have been well cooled. The necessity of doing this and of previously removing the flue-dust, which is sometimes very difficult to perform, is a great drawback to this, as well as to all corresponding processes. In fact Freytag's process has been abandoned again; at the best it could remove only a minor portion of the injurious constituents from the acid-smoke. (Schroeder and Haenisch, Chem. Ind. 1884, p. 118.)

Absorbing the acids by caustic lime, generally in the shape of a cream of lime, is one of the oldest and, if properly carried out, still one of the most efficient ways of removing the acid-smoke nuisance. Where the quantity of acids is but slight, and the manufacture in question is sufficiently profitable otherwise, this process is even now applicable, and if properly applied it does remove practically all the acids. The cream of lime should meet the gases in a finely divided state, either by flowing down properly-constructed towers, or, still better, by being converted into a spray by means of paddle-wheels or the like (comp. Rayner and Crookes' patent, E. P. 2678, 1475). That this leads to the desired effect even with the large quantity of SO_2 emitted in roasting blende, has been proved by working on the large scale in Upper Silesia (comp. Bernoulli, Fischer's Jahresb. 1880, p. 184). But unfortunately the expense of this process, where large volumes of acid gases are concerned, is very serious, more especially as nothing like the whole of the lime can be utilized for absorption, and the attempt of utilizing the product as bisulphite of lime (Hasenclever, G. P. 10710)

has failed (comp. Schroeder and Haenisch, Chem. Ind. 1881, p. 118).

According to Jensch (Fischer's Jahresb. 1889, p. 321) the deposit forming in the milk-of-lime towers contains so much lime that it can be used over again, and at least a product is obtained containing 37.7 per cent. lime, 38.4 SO_2 , 2.8 SO_3 , 4.1 CO_2 , &c., which is very useful as an addition to animal manure for the purpose of fixing the ammonia, in which respect it is equal to gypsum.

Limestone is very much cheaper than caustic lime, and is almost equally efficient if employed in the proper way; that is, if a very large surface of limestone is exposed to the acid gases, and if this surface is kept from being covered with a crust of sulphite by being constantly washed with a stream of water. Cl. Winkler has constructed a special arrangement for this purpose (G. P. 7174), which completely fulfilled its object at the Schneeberg ultramarine works. It consists of three brick chambers filled with large pieces of limestone, the roof being formed by plank covers perforated with many holes, through which water is kept running on to the limestone. The gases pass through these chambers successively and in regular rotation. The absorption of SO_2 is excellent, but as each cwt. of sulphur requires 3 cwt. of limestone, it is still too dear for most metallurgical purposes, especially as any utilization of the sulphur is out of the question.

Precht (E. P. 3443, 1881) employs for absorbing SO_2 from gaseous mixtures either *magnesium hydrate* or *aluminium hydrate*, especially the former. It is either spread upon trays moistened with water, or is brought into contact with the gases (previously cooled to 100°) in the state of a cream, in an apparatus provided with a mechanical agitator, or in columns like those employed for treating sulphuric acid by sulphuretted hydrogen (Chap. X.). This produces a crystalline precipitate of magnesium sulphite, besides a solution of magnesium sulphate. On heating the magnesium sulphate to upwards of 200° the SO_2 is split off, and can be condensed as such or converted into sulphuric acid, whilst magnesia remains behind, together with about 3 per cent. magnesium sulphate. The latter is heated with coals, and thereby converted into MgO , remaining behind, and a mixture of SO_2 and CO_2 , which is utilized in vitriol chambers [?]. M. Lyte (J. Soc. Chem. Ind. 1882, p. 165) gives a detailed description of this process

with diagrams. It has been tried at several places, but has been evidently found too little advantageous for most purposes.

Alumina is included in Precht's patent, but is less efficient than *magnesia*. Sometimes acid gases have been passed through layers of clay-slate (schist), whereby sulphate of alumina has been formed, but this process is evidently only practicable under special local circumstances.

Zinc carbonate or oxide was proposed by Schnabel (Fischer's Jahresb. 1882, p. 266), who had previously made manifold attempts at the Lautenthal smelting-works for treating the acid smoke, all without any sufficient success. Ultimately a process was adopted (G. P. 16860), consisting in passing the gases over basic zinc carbonate moistened with water. Zinc sulphate is formed, which, on heating (preferably mixed with coal), yields sulphurous acid, to be converted into sulphuric acid in lead-chambers, and a porous residue, consisting of a mixture of zinc oxide with basic zinc sulphate. Schnabel's apparatus is rather complicated, and the result not very satisfactory; the process is very troublesome to carry on, and costs much more than the value of the sulphuric acid obtained (a provisional protection, No. 5416, 1881, for this process was taken out in England by M. Lyte).

Fleitmann (G. P. 17397) passes the sulphurous gases, together with some air, through a kiln containing a mixture of *ferric oxide* and coal. The latter, in burning, yields the necessary heat, and at the same time reduces the Fe_2O_3 and SO_2 , so that FeS collects at the bottom (the success of this process is more than doubtful).

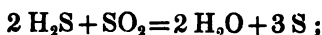
Metallic iron, moistened by water, was employed by Winkler (G. P. 14425), but was not found practicable for dilute acid gases. Thorp (E. P. 8862, 1889) again recommends towers filled with scrap-iron, and kept moist with water or a solution of ferrous sulphate, the temperature being kept at from 49° to 71° C.

Metallic copper or zinc, in very finely divided form, was tried at the Frankfort gold-parting works, but without sufficient success; but at the same works the following interesting process was worked out.

Rössler (Dingler's Journal, ccxlii. p. 278; Fischer's Jahresb. 1881, p. 184) showed that gaseous mixtures, containing, besides a large excess of air, far too little SO_2 and SO_3 for being treated in vitriol chambers and otherwise not treatable in any efficient manner, can be completely deprived of both the above acids by

forcing the gases, by means of a Körting's injector and a perforated coil of pipes, *underneath a column of water*, holding some *copper* in suspension or some *cupric salt* in solution. The cupric sulphate acts as a carrier of the oxygen of the air upon the SO_2 , and large quantities of sulphuric acid are formed in this way, so that this process might even be employed for manufacturing sulphuric acid. At Frankfort, however, it is carried out in this way, that the tank, into which the gases are passed, is always supplied with precipitated copper, from which by this process cupric sulphate is obtained without any expense. Rössler has also applied this principle to the treatment of ordinary acid-smoke (G. P. 22850), by combining a whole set of apparatus.

A special class of processes utilizes the reaction between *sulphur dioxide* and *hydrogen sulphide*, either both being in the state of gases, or the latter being in the nascent state as evolved from sulphides. The reaction in its simplest form is:

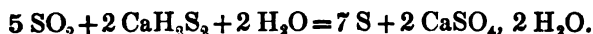


but, apart from the fact that polythionic acids are formed by secondary reactions, the above reaction is anything but complete with very dilute gases. Details about it will be given in a future volume in the chapter treating of the recovery of sulphur from soda waste; in this place it may suffice to mention that a patent founded upon the above reaction was taken out by Landsberg (G. P. 6364) in connection with the roasting of blende.

When sulphides are employed, the reactions are even more complicated, but the absorption of SO_2 can be made more complete. Cl. Winkler (Fischer's Jahresb. 1880, p. 245; more details in Chem. Ind. 1880, p. 126) describes a very interesting process for dealing with the gases from an ultramarine works containing much SO_2 . They were brought into contact with a solution of *sodium sulphide*, obtained from the sulphate going to waste in that manufacture, by reducing it with coal. The SO_2 is completely absorbed, with formation of sodium thiosulphate, or, in another modification, with formation of free sulphur; but on the large scale sodium tetrathionate was formed, which had to be decomposed by heating into sodium sulphate, SO_2 , and free sulphur. *Theoretically* nothing was consumed but coal, but evidently a very large amount of fuel must have been used in the various evaporations and furnace operations, with an amount of skilled labour out of propor-

tion to the value of the products obtained. After having been used from 1868 to 1877, the process just described was abandoned for a simple absorption by limestone moistened with water (p. 284). Even before Winkler, in 1864, Jacob had carried out for some years a similar process to that just described, employing either sodium or calcium sulphide, at Münsterbusch (Fischer's Jahresb. 1881, p. 181).

Calcium sulphide, proposed many years ago by Dumas, forms also the absorbing substance in Kosmann's process (G. P. 13123). By reducing calcium sulphate with coal and lixiviating a solution of calcium sulphydrate is obtained [?], which in very finely divided state is brought into contact with the gases containing SO_2 . The result is the formation of sulphur and gypsum:



The sulphur is extracted from the mixture by superheated steam, and the gypsum returns into the cycle of operations [it is very doubtful whether this would succeed!]. From further communications by Kosmann (Fischer's Jahresb. 1882, p. 270), it appears that the absorbing medium was afterwards prepared by boiling sulphur with milk of lime, that is, as the ordinary "liver of sulphur," and that the whole process was entirely in the experimental stage (from which it does not seem to have emerged).

Barium sulphide, which was experimentally tried at Freiberg, proved much too costly.

Vegetable charcoal is employed by A. H. Allen (B. P. 189, of 1879), who passes the gases, freed from dust, through drying-towers fed with sulphuric acid and then through columns filled with charcoal, previously ignited in a stream of nitrogen, where the SO_2 is retained, whilst the nitrogen passes on. By a vacuum or by heating to 300° – 400° , or by a combination of both, the SO_2 is to be driven out and utilized. (This process, apart from the prohibitory expense, is hardly practicable because the gases in question contain nearly always a large quantity of oxygen which will convert the SO_2 to a great extent into sulphuric acid within the pores of the charcoal.)

A totally different way of employing coal is used in one of the oldest processes for dealing with acid-smoke, namely, *passing the gases through red-hot coals*, in order to reduce the SO_2 to

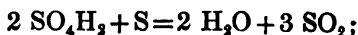
sulphur. This has already been mentioned in Vivian's pamphlet, "Proceedings of the Subscribers to the fund for obviating the inconvenience arising from the smoke produced by smelting copper ores" (London, 1833), and in a pamphlet of Reich's, describing the experiments made at Frankfort in 1858, and it has been proposed over and over again, with the same negative results. A new apparatus, by Schroeder and Haenisch (G. P. 33100), is said to give good results, nearly the whole of the SO_2 being reduced to S; but their process evidently works only with rich gases, and does not deal with those poor gases which concern us here.

8. PREPARATION OF SULPHUR DIOXIDE IN THE PURE STATE.

Formerly pure SO_2 , free from nitrogen and excess of oxygen, was required only in very few cases for industrial purposes. The methods employed for preparing that gas were various, one of the commonest being the action of concentrated sulphuric acid upon copper at a higher temperature. This is, of course, only applicable where there is a sale for the cupric sulphate formed, and is, moreover, hardly workable on a large scale. Cheaper and easier is the process of heating strong sulphuric acid with charcoal, when a mixture of SO_2 with CO_2 (and CO) is obtained:



The CO and CO_2 are harmless in many applications of SO_2 . Sulphur dioxide, quite free from other gases, is made by heating concentrated sulphuric acid with sulphur:



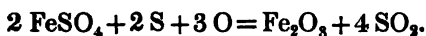
this can be done by running a slow stream of sulphuric acid on sulphur, heated to about 400° in an iron retort. It should, however, be noticed that melted sulphur acts very strongly upon cast iron; hence another process, privately communicated to me from a trustworthy source, would seem preferable. The operation is performed in a cast-iron pan, widening out at the top so that a lining of acid-resisting bricks can be put in it. Concentrated sulphuric acid is boiled with sulphur, which floats on the top and is kept by the brick lining from coming into immediate contact with the iron, whilst the lower part of the pan is fully exposed to the heating action of the fire.

Sulphur dioxide was made by the *Compagnie industrielle des*

procédés Raoul Pictet (G. P. No. 22365), and was purified in a special apparatus, utilizing the fact that the hydrates of SO_2 all crystallize at -10° , and that gaseous SO_2 at this temperature loses all its aqueous vapour. We refrain from describing this (somewhat complicated) apparatus, which is also described in the Journal of the Society of Chemical Industry, 1883, p. 413, as the condensation of liquid SO_2 is performed in a much simpler way by the Schroeder and Haenisch process, which in fact has caused the above-mentioned process to be abandoned.

P. Hart (E. P. 13950, 1885) prepares pure sulphur dioxide by acting with strong sulphuric acid, of spec. grav. 1.750, on finely ground iron sulphide, both being mixed in a cast-iron retort and heated to over 200°C. , when a steady stream of nearly pure SO_2 is evolved.

An old and well-known process for obtaining pure SO_2 is: heating ferrous sulphate with sulphur, with a little air, the reaction being:



This process has been made the subject of a new patent by Terrell (B. P. 5930, of 1884), who evidently lays the greatest stress on the ferric oxide remaining behind, which furnishes a good paint.

Ford's process (Am. Pat. 363457; Chem. Zeit. 1887, p. 721) consists simply in burning sulphur by means of air previously dried with sulphuric acid, and passing the gases through a worm, where, by cooling and pressure, liquid SO_2 is condensed. It is difficult to see any novelty whatever in this process.

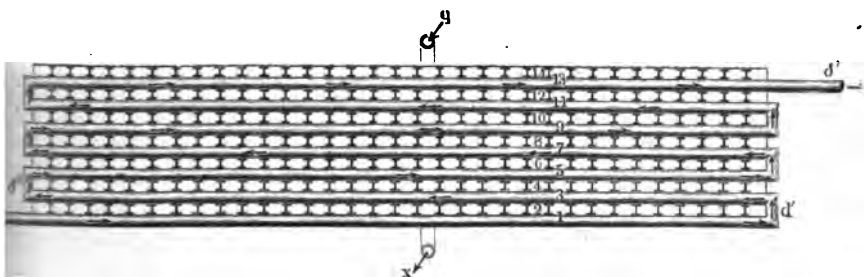
All other processes for preparing pure liquid sulphur dioxide have become obsolete by the process of Schroeder and Haenisch, which allows of preparing that substance in an extremely cheap way from gases containing down to 4 per cent. SO_2 , such as the gases obtained by roasting zinc-blende in an Eichhorn and Liebig furnace (p. 273), or in similar cases. It is unnecessary to say that richer gases are even better for this purpose. This process has made liquid sulphur dioxide a cheap article, manufactured on a large scale, and has made it possible to employ that substance for many purposes for which formerly only the ordinary impure gaseous SO_2 was available.

Schroeder and Haenisch's process (E. P. 2621, of 1883; 6404 and 6405, of 1885) consists in absorbing the SO_2 by means of

water in an ordinary coke tower, and expelling it again from the resulting weak solution by the action of heat, in such manner that the latent heat of the steam carried along is fully utilized, and ultimately a very small amount of coal is required. They describe their process, apart from the patent specifications, in the 'Chemische Industrie,' 1884, p. 120, where they point out that the removal of SO_2 from its solutions is very much facilitated by the simultaneous action of a current of air, and that in this way very much richer gases can be obtained than when burning even pure brimstone or the best sulphur ores, so that the sulphuric-acid chambers can be made very much smaller, and the expense of their own plant for retaining the SO_2 from poor gases and expelling it again is more than covered by the saving in cost of the vitriol-chambers. Schroeder and Haenisch's hopes of utilizing their process in this way have not been realized; the lowest strength at which it pays to treat the gases by the S. and H. process is 4 per cent. SO_2 , and at this strength the gas may be utilized directly in vitriol-chambers without actual loss of money. We shall, therefore, not give here the detailed descriptions and (somewhat scanty) diagrams found in the German patents and in the 'Chemische Industrie,' but quote from the later English and one of the later German patents the description of that shape of the apparatus which is intended for manufacturing liquid sulphur dioxide, and which is actually at work (of course with many modifications in details) at several places in Germany (Paper Trade Journal, 1888; Zeitschr. f. angew. Ch. 1888, p. 448). The burner-gases arrive in the flue *a a* (fig. 86), and after having lost part or most of their heat by passing underneath the lead pans *e e*, they pass into the coke-tower *b*, where they are treated with such a quantity of cold water that all the SO_2 is condensed, and only O and N pass out at *c*. The solution of sulphurous acid is run out by pipe *d*, and first passes through an apparatus, shown separately in fig. 87, where it receives a previous heating, and then successively through the closed lead pans *e e*, where the heating is continued by the action of the hot burner-gases acting in the flue *a a*. The apparatus, fig. 87, serves for heating up the cold acid solution by the heat of the spent liquor, resulting at a later stage of the process. It is built up by superposing a number of sheets of lead, 7 lb. per superficial foot, of considerable surface, corresponding to the quantity

of acid liquor to be treated. These sheets are combined in such manner as to form a corresponding number of shallow lead-chambers, about $1\frac{1}{2}$ inches deep, superposed over one another and connected with one another in the following way. The acid liquor flows through d into the bottom chamber from left to right; through a side connection d' , occupying the whole length of the lateral edge, it is conveyed into the third chamber, from here through δ'' into chamber 5, and thus further cools the 7th chamber, 9th, and so forth, issuing at δ . The chambers Nos. 2, 4, 6, 8, and so forth, serve in the same way for running down the hot spent liquor obtained at a later stage of the process. This liquor,

Fig. 87.



which enters at q , always flows in a direction at right angles to that of the acid liquor rising up in the alternate chambers, so that the connections for the spent liquor flowing down are situate in the front and back part of apparatus fig. 87. In order to prevent a sagging of the plates, strips of lead are arranged in each chamber as stays, running in each chamber in the direction of the current of liquor. The thin sheets of lead being good conductors of heat, the cold acid liquor on rising through chambers 1, 3, 5, 7, &c., is gradually heated up, whilst the hot spent liquor, descending through the intermediate chambers, gives off its heat. Of course there must be always a certain difference and loss of heat, depending upon the duration of contact, the depth of the liquid, and the speed of the current. With chambers of $1\frac{1}{2}$ or 2 inches depth, and counter currents lasting 10 or 12 minutes, and sufficiently large surfaces,

the difference of temperature will be about 10° ; that is, the cold acid liquor will be heated up from 15° to 18° C., whilst the hot spent liquor goes down from 95° to 25° C. The cold spent liquor is run to waste through *x*.

The heated-up acid liquor now travels successively through the covered lead pans *e e*, where the heating is continued as mentioned before, so that the boiling-point is attained. The gases and vapours here evolved are conducted through pipe *f* into the water-cooled worm *g*, and from here through pipe *h* into the tower *i*, where the last remaining admixture of moisture is taken out by dry calcium chloride or (preferably) by coke moistened with strong sulphuric acid. From here the dry sulphur dioxide passes through pipe *k* into the pump *l*. The liquor heated to boiling in the pans *e e*, which still contains some SO_2 , passes through pipe *m* into the column *n*, where the steam is to a great extent condensed by injection of cold water, whilst nearly dry SO_2 passes up in *p*, and thus equally gets into the worm *g* and further on into the pump *l*. The column *n* is shown in some detail, as described in a further patent by Schroeder and Haenisch (G. P. 36721), which refers to the separation of steam from its mixture with SO_2 , and as this is a matter of general importance, we shall give their statements at some length. It is not easy to separate large quantities of aqueous vapour from a mixture with gaseous SO_2 . Indirect cooling by outward application of cold water requires a very large leaden apparatus, and the effect is but partial, as the vapours pass without hindrance through the central parts of the worms or other kind of apparatus. Moreover the condensed water, unless the temperature of the cooling-apparatus is kept nearly at a boiling heat, carried down very much SO_2 . The new process effects the removal of the steam from the aforesaid gaseous mixture by direct injection of water, which certainly at first condenses a good deal of SO_2 . But if the acid solution thus formed is made in a systematic manner to meet the hot mixture of aqueous vapour and SO_2 , its temperature will be gradually raised and will ultimately attain boiling heat, and *pari passu* its percentage of SO_2 will decrease, so that at 100° it is nearly at zero. The following table shows the diminution of the percentage of SO_2 with the rise of temperature:—

Percentage of a saturated solution of SO_2 :—

At 20° C. = 8·6	per cent. SO_2 .
„ 30° C. = 7·4	„ „ „
„ 40° C. = 6·1	„ „ „
„ 50° C. = 4·9	„ „ „
„ 60° C. = 3·7	„ „ „
„ 70° C. = 2·6	„ „ „
„ 80° C. = 1·7	„ „ „
„ 90° C. = 0·9	„ „ „
„ 100° C. = 0·1	„ „ „

If the injection of water is so adjusted that the liquid running off is at a temperature of 95° or 100° C., the latter cannot, as shown by the preceding table, carry away any considerable quantity of SO_2 . On the other hand, if the way traversed is long enough, the steam must be completely condensed by the cold water injected.

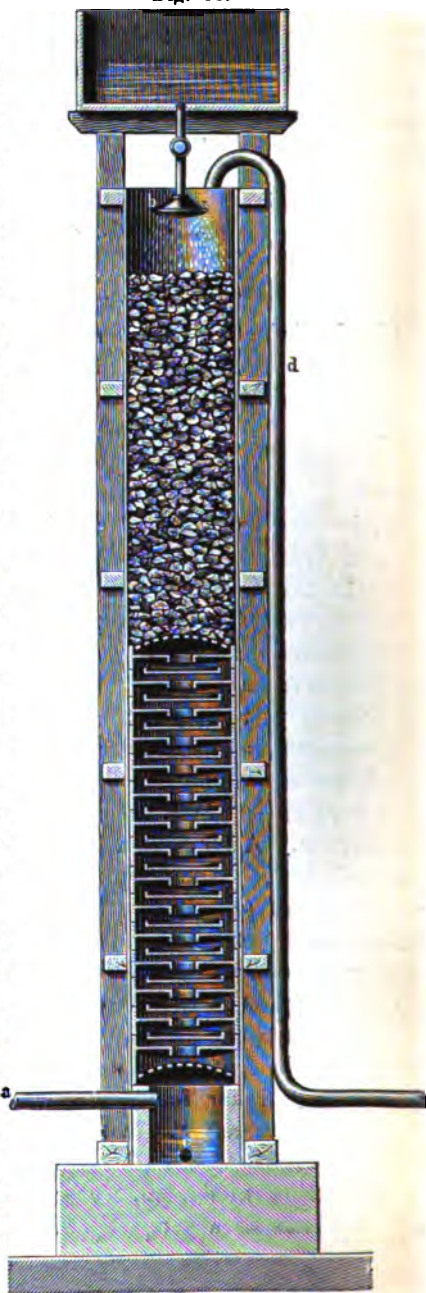
This process is carried out in the apparatus shown in fig. 88, viz., a leaden column, filled in the lower part with stoneware diaphragms, in the upper part with coke. The mixture of steam and SO_2 enters through pipe *a* and rises in the tower. Cold water is injected by the rose *b*, condensing both water and SO_2 , and flowing down as an aqueous solution of sulphurous acid. On reaching the lower parts, it meets continually new quantities of hot gases and vapours, and arrives at the bottom 100° C. hot. In this it yields up again the SO_2 absorbed higher up, and at the bottom pipe *c* carries off both the injected water and that condensed from the steam. After some time of working, and with proper regulation of the feed, the temperature of the water from the top downwards rises regularly to a boiling heat, and its percentage of SO_2 diminishes at the same ratio; but the quantity of SO_2 in the upper region is so considerable that the injected water cannot retain it all, and pipe *d* carries away a continuous stream of gaseous SO_2 deprived of steam. The dish shape of the stoneware parts in the lower half of the tower has the advantage of retaining the descending liquor for some time, and exposing it to the heat of the rising steam; but instead of this, coke may be used all over, if the tower is made high enough.

Returning to fig. 86, we see that the water condensed in the worm *g* finds its way equally into column *n*, and is deprived of its

SO₂ there. The hot spent liquor runs off at the bottom by pipe *g*, and is utilized, as explained before, for heating up the cold acid liquor in the apparatus, fig. 87, where the entrance to the pipe *g* is visible. In order to regulate the compression of the gaseous sulphur dioxide to a liquid, a taffeta bag (*r*) is interposed in pipe *k*, and the motion of pump *l* is regulated according to the size of this bag. The compressed gas enters through *s* into the worm *t*, and is liquefied there; from *t* the liquid runs into the wrought-iron boiler *u*, from which it is drawn off into the iron bottles *v* or into tank-waggon. In order to get rid of the carried-along portions of oxygen and nitrogen, the boiler *u* is provided with an outlet pipe *w*, connected with *u* by a valve; the gases from here are conducted back into the absorbing-tower *b*.

The liquid sulphur dioxide is sent out in iron cylinders (bottles) holding 1 or 2 cwt. each, or in tank-waggon of 10 tons capacity. The former are shown in figs. 89 and 90. When sent out, the outlet valve is protected by a cap *a*. Before use this is removed, as well as the small cap fixed on the neck *b*. If now the pier of

Fig. 88.



the screw-valve *c* is turned by means of a key, the sulphur dioxide escapes in gaseous form through the opening in *b*. The stuffing-box or the whole valve must *not* be removed. After a time the evaporation of SO_2 lowers the temperature to -10°C , so that no more gas is given off till the apparatus has taken up heat from without.

If the sulphur dioxide is to be got out in the liquid form, the vessel is put on its side (fig. 90) in such a position that neck *b* is at the top side. The pressure of its vapour now forces the SO_2 out of *b*. The bent tube within the vessel admits of emptying it entirely of liquid SO_2 . This substance can be conveyed away by a lead pipe, screwed on to *b*, or even by an india-rubber pipe. The

Fig. 89.



Fig. 90.



bottles are tested to 50 atmospheres pressure, so that there is no danger whatever in their transit, as the vapour-tension of SO_2 amounts to:—

0 atmosphere overpressure at -10°C .				
0.53	"	"	"	0°
1.26	"	"	"	$+10^\circ$
2.24	atmospheres	"	"	20°
3.51	"	"	"	30°
5.15	"	"	"	40°

Still, it is advisable not to keep the liquid in a place whose temperature may rise upwards of 40°C .

9. DRAUGHT-PIPES AND FLUES.

The flues leading the burner-gases from the kilns into the chambers or into the Glover towers may be constructed of brickwork only so far as the gases keep hot enough not to allow any moisture whatever to condense, that is especially in upright flues and flue-dust chambers. From this point they must be made of cast-iron, and further on, when they have got cooler, of lead.

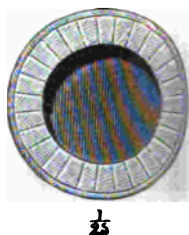
The gas, which goes away red-hot from the burners, must necessarily be *cooled down* to the temperature of the chambers, say 60° or 80° C.; otherwise the first chamber would be very quickly destroyed. This cooling was formerly effected by conveying the burner-gas in very long flues of cast-iron, or partly of cast-iron, and, when partially cooled, of lead. Such cooling-flues were made up to 300 feet long.

The cast-iron pipes are suitably shaped, as shown in fig. 91, in order that the upper half may be replaced independently of the lower one, or taken away for cleaning; the latter can also be done by

Fig. 91.



Fig. 92.

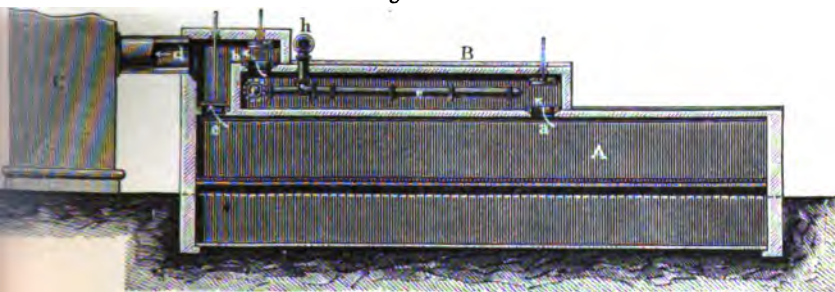


means of man-holes. For a set of from 12 to 18 burners a pipe of 2 feet diameter is sufficient; but they are sometimes made upwards of 3 feet in diameter. Sometimes they are lined with fire-bricks, as shown in fig. 92; the cooling in this case is very imperfect and the cost higher. Occasionally, in very large works, square or oblong flues of wrought or cast-iron are found. Brick flues (for perpendicular shafts or for flue-dust chambers) are made of bricks boiled in tar, and set with tar and sand. Earthenware pipes mostly crack too quickly.

Perpendicular stacks or pipes act as a sort of chimney, and they are therefore carried up nearly to the top of the chambers, where there is no Glover tower. Sometimes these pipes were

outwardly cooled by water, and even very complicated contrivances were met with for this purpose. It has long been recognized that the only rational way of cooling the burner-gas is this: taking away its heat for some useful purpose, and this is almost everywhere done in the Glover tower (Chap. VIII). Apart from this, the heat of the burner-gas is sometimes utilized for concentrating acid in lead pans (Chaps. IV. and XI.). Sometimes other ways of disposing of this heat are employed. Thus at the manure-works of Messrs. H. and E. Albert, at Biebrich-on-the-Rhine (see fig. 93), each pyrites-kiln A is surmounted by a gas-chamber B; the burner-gases enter by the holes *a*, provided with shut-off valves, and through similar openings (*b*) get into the pipe *d*, leading to the Glover tower C; a third opening (*c*) permits sending the gas direct into *d* and C. In each of the chambers B there are horizontal cast-iron pipes (*e*), branching off from a main pipe *f*, into which air is forced by a fan-blast. This air, being exposed to the hot burner-gases, becomes hot itself and leaves the chambers, in order to be carried away by the main pipe *h*. This heated air is then conveyed to drying-stoves,

Fig. 93.



where the superphosphate is dried by its action. At Albert's works the temperature of the air is brought to $100^{\circ}\text{C}.$, but it may be kept cooler or hotter (up to 135°) by regulating the speed of the fan-blast. The burner-gas, entering through *d* into the Glover tower C, is still hot enough to do all the concentrating and denitrating work required; the Glover towers are less overheated and require less repairs than formerly; the acid flows from them only at 115° – 120° , against 140° as before the new arrangement, and requires less cooling for the Gay-Lussac towers. The saving in

coals for the drying-stoves is 5 tons per diem (comp. the description, with further diagrams, in *Zeitschr. f. angew. Chemie*, 1889, p. 287; also E. P. of Albert, Fellner and Ziegler, No. 15980, of 1888).

Flue-dust.

In the gas-flues and draught-pipes *flue-dust* is always deposited, much more when smalls are burnt than with lump ore, especially in furnaces where the small ore is moved about. In such cases special dust-chambers are indispensable, as has been remarked in the description of those furnaces. Even with large lumps the flues and pipes must be cleaned out from time to time, as they would otherwise be stopped up entirely. At some factories this is done monthly, at others more rarely. If the deposit is allowed to remain too long, it hardens into a stone-like mass, which cannot be got out without stopping the process.

The composition of this deposit varies, of course, very much; and even its external aspect varies from that of a dry, light dust, to that of thick, strongly acid mud. Clapham analyzed such a deposit, from a not quoted source (Richardson and Watts, *Chem. Technol.* i. 3, p. 70), and found:—

Sand, &c.	2·333
Lead oxide	1·683
Ferric oxide	3·700
Cupric oxide	trace
Zinc oxide	trace
Arsenious acid	58·777
Sulphuric acid	25·266
Nitric acid.....	trace.
Water	8·000
	<hr/>
	99·759

D. Playfair (*Chem. News*, xxxix. p. 245) has examined flue-dust from pyrites-kilns, in which he found chiefly arsenic, antimony, lead, copper, and iron; of thallium 0·002 to 0·05, of tellurium and selenium 0·001 per cent. was present. He describes in detail the analytical methods employed.

Reich ('*Erdmann's Journal*,' xc. p. 176) found in the Mulden

Works a crystallized deposit consisting of equal molecules of arsenious acid and sulphuric acid.

In other cases the deposit is dry dust, mostly consisting of mechanically conveyed pyrites-dust, better burnt than that within the burner itself (Bode, 'Beiträge,' p. 41), and nearly always containing so much arsenic that its crystals can be seen with the naked eye.

H. A. Smith ('Chemistry of Sulphuric-Acid-making') found in it 46·36 per cent. of As_2O_3 , along with a large quantity of sulphur in the pasty condition—the latter, of course, formed by sublimation from pyrites.

The flue-dust is also a principal source of *thallium*, as we shall see; and when *selenium* occurs in the pyrites it is found in the flue-dust.

The flue-dust from the roasting of blende is, of course, quite differently composed from that formed in burning pyrites. Such flue-dust contains (Fischer's Jahresb. 1882, p. 273) :—

	I.		II.
Zinc oxide insoluble	8·40	} 26·20	8·20
Ditto in soluble combination	17·80		12·00
Ferrous oxide, soluble	2·16		2·52
Ferric oxide, ditto.....	2·40		4·20
Lead oxide.....	3·38		4·26
Sulphuric acid, insoluble	6·46	} 26·89	8·04
Ditto soluble.....	20·43		18·84
Water.....	6·59		9·00
Residue (chiefly ferric oxide)	31·80		32·42
	<hr/>		<hr/>
	99·42		99·48

Bellingrodt (Chem. Zeit. 1886, p. 1039) has found in the flue-dust from roasting blende at Oberhausen (Rhenish Prussia) a sufficient quantity of mercury to make its recovery profitable.

Where the quantity of flue-dust is very large, as is generally the case with arsenical ores, and with some of the burners for pyrites smalls, the ordinary dust-chambers, which form simply enlargements of the gas-flue, as seen for instance in Schaffner's shelf-burners (p. 256), are not sufficient, and special contrivances must be adopted here. This matter has been thoroughly worked out in the lead-smelting works and other metallurgical establish-

ments, and a large number of apparatus has been constructed for this purpose. A very complete synopsis of this is given in the pamphlet by C. A. Hering: '*Die Verdichtung des Hüttenrauchs*' (Stuttgart, 1888), pp. 8 to 36. Many of the contrivances employed at lead-works, &c., are unsuitable for pyrites on account of being made of iron. But the general principles remain the same: the flue-dust must be made to deposit by cooling, by retarding the speed of the gaseous current and by offering to it large surfaces to which it can attach itself. All these conditions are more or less fulfilled by making the gas-flues sufficiently long and wide, but this is not sufficient for "bad cases," especially for arsenical ores. The case is here complicated by the fact that the cooling of the gas may be injurious to the chamber process, and that the long flues, especially those carried in a zigzag way or provided with "baffle-walls," interfere very seriously with the draught. The latter disadvantage has been greatly lessened since it has been recognized that it is unnecessary to carry the gases in

Fig. 94.

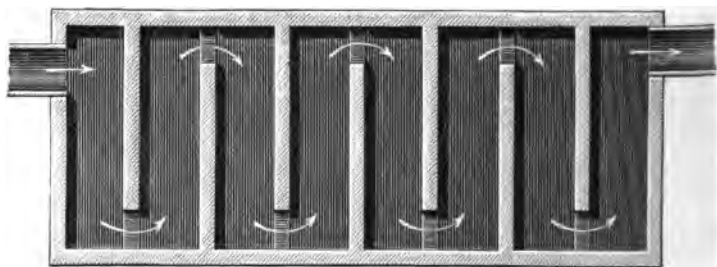
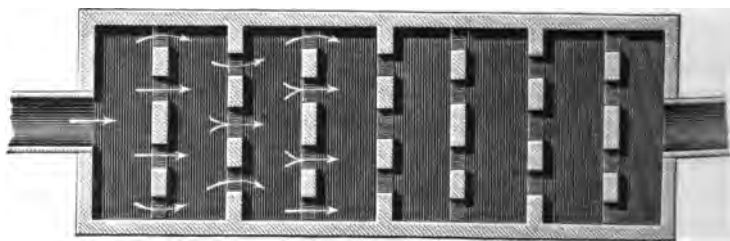


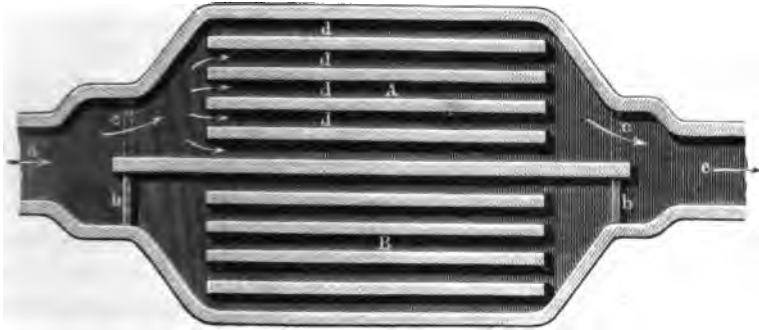
Fig. 95.



flues like those sketched in figs. 94 and 95 (in the former the diagram may be taken either as plan or elevation), where the

current of gas is constantly checked by meeting solid surfaces, but that the surfaces may be disposed in the direction of the current itself, where they give occasion to the dust to deposit on them without interfering with the draught. Fig. 96 shows how

Fig. 96.



this can be done in such manner that the flue-dust can be removed without interfering with the process. The gases arriving through *a* are, by means of dampers, sent either through chamber A or B. In the present case, the dampers *b b* being closed, the gases travel through A. Each chamber is divided into several longitudinal channels by thin partitions *d d*, made of masonry, fireclay slabs, lead, or other suitable material. The gas thus travels in parallel streams, without any check than that of the indispensable friction, and the streams collect again into one, issuing at *e*. When chamber A is too much choked up by dust, the dampers *b b* are opened, the dampers *c c* are shut, and the gases now travel through B, giving an opportunity to clean out chamber A by means of suitable man-holes.

In many cases, where very large quantities of flue-dust have to be dealt with, the gases must be cooled artificially. Thus it is done at the Freiberg works by a special kind of lead flue, cooled by water, as sketched in figs. 97 and 98, where the first represents a longitudinal section on the line A B, the second a sectional plan on the line C D. The sides of the flue are formed by a number of oblong pipes, *a a*, joined together at their narrow ends. On the top there is a shallow trough, *b*, supplied with a constant stream of water, which trickles down through holes, shown in the diagram, into the spaces *a a*, and from these through other

holes into the common channel *c*, running lengthways. The bottom of the flue is not water-cooled, but as it rests on the small pillars *d d*, it is exposed to the action of the air. These flues are very expensive to build, but they have been found to do their

Fig. 97.

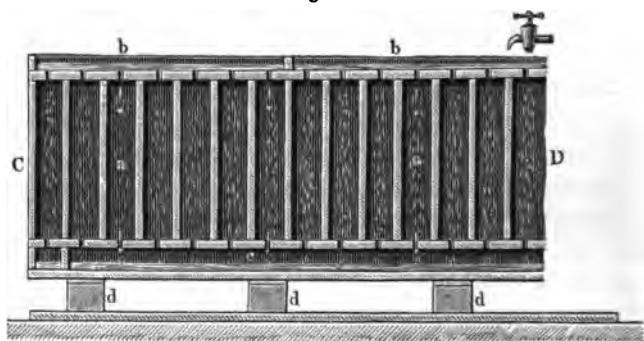
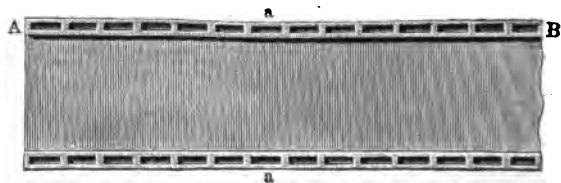


Fig. 98.



work very well indeed, and they cause next to no repairs (detailed in the 'Freiberger Jahrbuch,' 1879, p. 151, table xii.). Of the 2 or $2\frac{1}{2}$ per cent. of arsenic contained in the Freiberg ores, by far the greatest portion (97 per cent.) is condensed in these long flues, where the gases are ultimately cooled down to the temperature of the outer air.

CHAPTER V.

THE BURNER-GAS.

THE *composition of the gas generated in the burners* has been accurately calculated by Schwarzenberg, both for brimstone and for pyrites; and we shall in the first place give his calculations, in which at the same time the *draught* is taken into account, such as is required in normal circumstances.

1. *Composition of the Burner-gas, Draught, and Quantity of Air necessary in burning Brimstone.*

The draught by which air is introduced into the burners, and by which the mixture of gases formed therein, and ultimately that remaining after the formation of sulphuric acid, is carried through the lead-chambers and out of them, is of very great importance for the way in which the process goes on.

The draught is generated by several causes, of which the first is the heat of the gaseous mixture contained in the vertical tube leading from the sulphur-burner to the lead chambers. As the density of it is twice as great as that of atmospheric air, it might be supposed that the gaseous mixture formed in the burner was not lighter than the air. We shall therefore compute its specific gravity. As constants for this and the following calculations we shall use the following figures:—

At 0° C. and 760 millims. mercurial pressure :

	gram.
1 litre of dry atmospheric air weighs...	1.2932
1 " " oxygen	1.4298
1 " " nitrogen	1.2562
1 " " sulphur dioxide	2.8731
1 " aqueous vapour	0.804343

Now 1 vol. oxygen gas, on combining with sulphur, forms 1 vol. SO_2 , which further requires $\frac{1}{2}$ vol. of oxygen to form SO_3 . For each 14 vols. SO_2 , containing 14 vols. O, another 7 vols. O are thus necessary for the transformation into SO_3 . All this oxygen is introduced into the burner as atmospheric air, containing in 100 vols. 21 vols. oxygen and 79 vols. nitrogen. The above $14 + 7 = 21$ vols. O therefore introduce 79 vols. of nitrogen into the burner, and the gaseous mixture there formed thus theoretically ought to contain

$$\begin{array}{r}
 14 \text{ vols. } \text{SO}_2 \\
 7 \quad \text{,,} \quad \text{O} \\
 79 \quad \text{,,} \quad \text{N} \\
 \hline
 100
 \end{array}$$

Experience, however, has taught that for a good working process a further excess of oxygen is required, in the case of brimstone amounting to 5 vols. upon 95 vols. of the nitrogen entering and again leaving the chambers.

If we call the unknown volume of this excess oxygen $= x$, it must carry along $\frac{79}{21}x$ vols. N. To this are added 79 vols. N, entering along with the 21 vols. O required for forming 14 vols. of SO_2 and converting them into SO_3 . The volume of the total N and of the excess oxygen required in practice for each 14 vols. of SO_2 introduced into the chambers thus amounts to

$$79 + \frac{79}{21}x + x = 79 + \frac{100}{21}x.$$

x was stated to form 5 per cent. $= \frac{1}{20}$ of this volume.

We have thus the equation

$$x = \frac{1}{20} \left(79 + \frac{100}{21}x \right) = \frac{79}{20} + \frac{5}{21}x.$$

From this follows

$$x - \frac{5}{21}x \text{ or } \frac{16}{21}x = \frac{79}{20},$$

$$x = \frac{79 \times 21}{20 \times 16} = 5.18 \text{ vols. ;}$$

that is, besides the theoretical quantities of gas mentioned above,

another 5.18 vols. of oxygen, along with the corresponding $5.18 \times \frac{79}{21} = 19.50$ vols. of nitrogen, are necessary. The gaseous mixture formed in the sulphur-burner accordingly ought to contain upon each

$$\begin{array}{rcl}
 & 14 & \text{vols. of SO}_2, \\
 7 + 5.18 & = & 12.18 \quad ,, \quad \text{O, and} \\
 79 + 19.50 & = & 98.50 \quad ,, \quad \text{N.} \\
 \hline
 & 124.68 & \text{vols.}
 \end{array}$$

From this the following composition for 1 litre of this gaseous mixture is computed :—

$$\begin{array}{rcl}
 0.1123 & \text{litre SO}_2, \\
 0.0977 & ,, \quad \text{O} \\
 0.7900 & ,, \quad \text{N} \\
 \hline
 1.0000 & ,,
 \end{array}$$

That is to say: *The normal quantity of SO₂ in burner-gas from brimstone-burners is 11.23 per cent. by volume.*

According to the densities of the single gases mentioned above, 1 litre of this mixture at 0° C. and 760 millims. mercurial pressure must weigh

$$0.1123 \times 2.8731 + 0.0977 \times 1.4298 + 0.7900 \times 1.2562 = 1.4547 \text{ grm.}$$

Now gases, on their temperature being raised, the pressure remaining the same, for each 1° C. expand by $\frac{1}{273}$ of the volume occupied at 0°. 1 litre of 0° C. thus at t° C. (the pressure remaining unchanged) furnishes

$$1 + \frac{t}{273} = \frac{273+t}{273} \text{ litre.}$$

If we assume the temperature of the gaseous mixture in the pipe leading from the burners = 100° C., which no doubt is below the truth, there would be formed

$$\frac{273+100}{273} = 1.3663 \text{ litre}$$

from each litre at 0° C. and equal pressure; and these, of course would equally weigh 1.4547 gram at a pressure of 760 millims.

1 litre of the gaseous mixture at 100° C. and 760 millims. pressure thus weighs

$$\frac{1.4547}{1.3663} = 1.0647 \text{ gram.}$$

With this we shall compare the weight of air. 1 litre of atmospheric air at 0° and 760 millims. pressure weighs 1.2932, and at 20° and equal pressure furnishes

$$\frac{273 + 20}{273} = 1.0733 \text{ litre;}$$

$$\text{it therefore weighs } \frac{1.2932}{1.0733} = 1.2049 \text{ gram.}$$

Thus atmospheric air at 20° is much heavier than the gaseous mixture in the sulphur-burner. Even at an extraordinarily high atmospheric temperature, such as 35°, the weight of the latter still exceeds a good deal that of the gas; for, as $\frac{273 + 35}{273} = 1.1282$,

1 litre air at 35° and 760 millims. is

$$\frac{1.2932}{1.1282} = 1.1463 \text{ gram.}$$

The aqueous vapour always present in the air was not required to be taken into account, since by its expansion in the heat of the burner it can only increase the difference between the weight of the gas and that of the air.

Owing to the fact that the gaseous mixture in the vertical pipe of the sulphur-burner is lighter than air, it must issue out of the top of the pipe into the chamber with a speed corresponding to the excess pressure of the atmosphere acting upon it from below. It must therefore by itself exercise a pressure upon the gas in the lead chamber. Its speed or the draught increases with the height of the vertical pipe; and the latter therefore ought to enter into the chamber-side as high up as possible. By thus securing more than sufficient drawing-power the supply of air is secured in any case; and its excess can always be moderated by narrowing the area of the inlets.

A second cause of draught is the formation of sulphuric acid itself, as the space occupied by the consumed gas cannot remain empty, and must at once be filled again. The condensation of the gas to sulphuric acid thus acts as an aspirator.

A third cause of draught is the vertical pipe taking the gas away from the last lead chamber, or the chimney with which it is connected. As the gas in these contains all the nitrogen introduced into the chambers with only 5 per cent. of oxygen, as it is saturated with aqueous vapour, and as it is usually warmer and never can be colder than the atmospheric air, it must necessarily be lighter than the latter: this is evident without any calculation.

If the nitrogen-acids are not recovered by a special process, to be explained later on, the gas certainly contains a little of those acids and of sulphurous acid, by which their specific gravity is somewhat increased. We shall, however, see that that influence is very slight, and does not materially interfere with the causes producing a decrease of the specific gravity.

The draught produced by all the above-mentioned causes regulates the quantity of air which can enter the apparatus by openings of a certain size. We have already seen that we must not introduce the exact quantity of air required for transforming the burnt sulphur into SO_3 , but a certain excess, which we have calculated = 5.18 vols. of oxygen upon each 14 vols. of SO_2 . With this, for each 14 vols. of SO_2 ,

$$14 + 7 + 5.18 = 21 + 5.18 = 26.18 \text{ vols. oxygen,}$$

$$\text{and } 79 + 19.50 = 98.50 \text{ ,, nitrogen,}$$

$$\text{together } 124.68 \text{ ,, atmospheric air,}$$

must be introduced into the chambers. From this it follows that for each vol. SO_2 $\frac{124.68}{14} = 8.906$ vols. of air are required. Now 1 litre of SO_2 at 0° and 760 millims. pressure weighs 2.8731 grams, and SO_2 consists of equal parts by weight of sulphur and oxygen. Accordingly 1 litre of SO_2 at 0° and 760 millims. contains

$$\frac{2.8731}{2} = 1.43655 \text{ gram sulphur,}$$

$$\text{and } 1.43655 \text{ ,, oxygen.}$$

Thus for each 1.43655 gram of sulphur burnt 8.906 litres air at 0° and 760 millims. are required. Since

$$1.43655 : 1000 :: 8.906 : x,$$

x 2

each 1000 grams or 1 kilogram sulphur requires $\frac{8906}{1.43655} = 6199$ litres air at 0° and 760 millims. pressure to be introduced into the sulphur-burner, weighing $6199 \times 1.2932 = 8017$ grams or 8.017 kilograms.

For calculating the volume of air at different temperatures and pressures we must introduce the well-known formula: viz., for a temperature t° C. and a barometrical height b (in millimetres) the volume V (at 0° and 760 millims.) becomes

$$\frac{(273+t) V \times 760}{273 \times b}.$$

For instance, at 20° and 760 millims. the calculation shows 6653 litres.

All the above calculations refer to dry air; but as the atmosphere is never free from moisture, we must take this into account. If a gas is saturated at the pressure b with aqueous vapour, its own tension is diminished by that of the vapour, and becomes $b-e$, if e be the tension of the vapour alone; so that the mixture now has the same tension as the gas previously had by itself. Thus from the volume $\frac{(273+t) V \times 760}{273 \times b}$ the new volume V' for gas saturated

with moisture calculates as $V' = \frac{(273+t) V \times 760}{273 (b-e)}$.

The volume V' of the 6199 litres of dry air at 0° and 760 millims., on being saturated with moisture and the temperature raised to 20° C. (at which aqueous vapour has a tension of 17.391 millims. of mercury), calculates for 760 millims. pressure as

$$\frac{(273+20) \times 6199 \times 760}{273 (760-17.391)} = \frac{293 \times 6199 \times 760}{273 \times 742.609} = 6809 \text{ litres.}$$

The above calculations have thus shown that each kilogram of pure sulphur burnt for producing sulphuric acid requires a supply of

6199 litres dry air at 0° C. and 760 millims. pressure,
of $6199 + 454 = 6653$ „ „ 20° „ „ „
„ $6653 + 156 = 6809$ „ air saturated with moisture at 20° C. and
760 millims. pressure.

The last increase of 156 litres is only fully realized in the exceptional case of air completely saturated with moisture. As this

increase is only 2·34 per cent. of the volume of the necessary dry air, whilst, according to the calculation on p. 304, about 24·68 per cent. of the theoretical quantity of air (that is, more than ten times as much) is introduced in excess, the changes in the moisture of the air and the differences of volume resulting therefrom are of no practical consequence. We shall therefore not enter into a calculation of the differences caused by the real percentage of moisture in the air.

Of course the volume of air necessary for a certain consumption of sulphur is also dependent upon the elevation of the site above the level of the sea, which regulates the mean barometrical pressure. Thus at Munich a quantity of air occupies a space larger by 5·5 per cent. than the same quantity at Marseilles (or Widnes).

It is easy to introduce the minimum of air required for proper work. But this is not all; an excess of air is just as hurtful as a deficiency, although not to the same extent. Air in excess cools the gas, and thus may sometimes interfere with the process; it fills a portion of the chamber-space and renders it inoperative; it dilutes the gas and weakens the energy of the chemical action. The regulation of the supply of air must therefore be accurate, and must be adapted to the frequent variations in the state of the atmosphere. This must be done by great attention in enlarging or diminishing the openings serving for introducing the air and for taking away the gas. By either means the supply of air can be diminished; but it is not indifferent which of them is selected. By the latter the draught acting upon the contents of the chambers at the end of the apparatus, by the former the pressure upon the contents of the chambers at the beginning of the apparatus is lessened. In the latter way the pressure inside the chambers is increased; in the former way it is diminished. Accordingly, if the chimney-draught is too much cut off, the gas issues forcibly from any openings in the chambers, &c., whilst the air may enter properly by the holes in the front of the sulphur-burners. If, however, these latter are stopped up too far, the chambers suck in air in any places not completely closed against the atmosphere.

The draught can also be increased in two different ways, viz., by enlarging the opening in the exit-tube, or by increasing the inlet-holes in the door of the burner. Then the chambers, if the exit-tube is not sufficiently closed, suck in air; if, on the other hand, the inlet-openings are too wide, gas is forced out from any leaks in

the chambers by the excess pressure. This is especially noticed when the doors are opened for charging. Both can be avoided by arranging a certain proportion between the inlet and the outlet openings. Usually (according to Schwarzenberg) the area of the latter is two-thirds of that of the former. For the changes of draught made necessary by the variations in the state of the atmosphere no certain rules can be given; observation and practice must come into play here. In well-arranged works, however, this is not left to chance, but the supply of air is checked by regularly estimating the oxygen in the escaping gas, as we shall see later on.

2. Composition of the Burner-gas, Draught, and Quantity of Air necessary in burning Pyrites.

The same considerations as influence the draught in sulphur-burners are also valid in burning pyrites. But the proportion of air required is very much altered. We shall calculate this for pure iron bisulphide. This body consists of

1 at. iron.....	Fe=	56=46.66 per cent.
2 „ sulphur ...	S ₂ =	64=53.33 „
<hr/>		
	FeS ₂ =	120

Although on burning dense pyrites sometimes the iron is not all oxidized up to Fe₂O₃, and a little magnetic oxide, Fe₃O₄, is formed, we must suppose the complete conversion of iron into Fe₂O₃ as the normal state to be aimed at for complete utilization of the sulphur. Consequently 2 mols. or 240 pts. of FeS₂ require 3 atoms=48 pts. O for oxidizing the iron, and another 8 atoms=128 pts. O for burning the S into SO₂. Altogether 11 atoms=176 pts. oxygen are necessary for burning, and another 4 atoms of oxygen=64 pts. for changing the formed 4 mols.=256 pts. of SO₂ into SO₃. From this we calculate:—

1. That for each thousand parts of FeS₂,

200 pts. oxygen are required for oxidizing the iron,	
533½	„ „ „ forming SO ₂ ,
266½	„ „ „ oxidizing this to SO ₃ ,
<hr/>	
1000	„ in all ; and,

2. That for each 100 pts. of sulphur employed as FeS_2 ,

375	pts. oxygen must be supplied for oxidizing the Fe,
1000	" " " forming SO_2 ,
500	" " " oxidizing this to SO_3 .

Since 1 litre of air at 0° and 760 millims. pressure weighs 1.4298 gram, at this temperature and pressure

375	grs. O give 262.3 lit., mixed in the air with 986.7 lit. N,
1000	" " 699.4 " " " 2631.1 "
500	" " 349.7 " " " 1315.5 "
<hr/>	
1875	" " 1311.4 " " " 4933.3

Accordingly, theoretically, for each kilogram of sulphur consumed as FeS_2 $1311.4 + 4933.3 = 6244.7$ litres air at 0° and 760 millims. pressure must be supplied.

Now here also an excess of oxygen must be used, even larger than in the case of brimstone, which Schwarzenberg states to amount to 6.4 per cent. by volume in the gas leaving the chambers. If we call the unknown volume of oxygen in excess to be introduced for each kilogram of S employed as FeS_2 , x litre, the volume

of nitrogen accompanying it is $\frac{79}{21} x$ litre. Both together and the

4933.3 litre N introduced along with the O requisite for combustion and formation of SO_3 form the gaseous mixture escaping at the end, the volume of which is therefore

$$4933.3 + x + \frac{79}{21} x = 4933.3 + \frac{100}{21} x.$$

As x is $\frac{6.4}{100}$ of this volume, we have

$$x = \frac{6.4}{100} \left(4933.3 + \frac{100}{21} x \right),$$

$$x = 454.1$$

Accordingly for each kilogram of S burnt as FeS_2 , apart from the theoretical 6244.7 lit. air, another 454.1 lit. oxygen along with $\frac{454.1 \times 79}{21} = 1708.4$ nitrogen—that is, 2162.5 lit. air—altogether 8407.2 lit. air at 0° and 760 millims. pressure, have to be introduced.

Now we have found that each kilogram of free sulphur (brimstone) requires 6199 litres air at 0° and 760 millims. ; consequently a certain quantity of sulphur, burnt as FeS_2 , requires

$$\frac{8407.2}{6199} = 1.356 \text{ times}$$

as much air as if burnt in the free state.

This is not quite the proportion of the gas *as it enters the chambers*. For on burning FeS_2 , a portion of the oxygen remains behind with the iron, whilst on burning brimstone the whole quantity of air gets into the chambers, and at equal temperature and pressure retains its volume, since oxygen on combining with S to SO_2 does not change its volume.

The 8407.2 litres air entering the burner for each kilogram of sulphur burnt as FeS_2 , furnished the following quantities of gas, calculated for 0° and 760 millims. :—

699.4	lit. SO_2 generated from the same volume of O,
349.7	,, O required for transforming SO_2 into SO_3 ,
454.1	,, O as excess,
4933.3	,, N accompanying the theoretically necessary oxygen,
1708.4	,, N ,, ,, excess of oxygen,

8144.9	lit. containing 699.4 lit. SO_2 ,
803.8	,, O,
6641.7	,, N.

Consequently, in the case of burning pyrites, 100 volumes of the normal gaseous mixture on entering the chamber ought to consist of

8.59	vol. SO_2 ,
9.87	,, O,
81.54	,, N.

In many factories the sulphurous acid is much below 8.59 per cent.; sometimes not above 6 per cent. of the volume of the gas. In that case so much less acid is made in the same chamber-space, unless the formation of sulphuric acid is increased by a larger consumption of nitre.

1 litre of the above gas at 0° and 760 millims. weighs

$$0.0859 \times 2.8731 + 0.0987 \times 1.4298 + 0.8154 \times 1.2562 = 1.4122 \text{ grm.,}$$

whilst the 1 litre of the gas resulting from the combustion of brimstone, according to our former calculation, weighs 1·4547. The former being, under equal conditions, lighter than the latter, consequently gives stronger draught.

For a certain quantity of sulphur, burnt as FeS_2 , $\frac{8144\cdot9}{6199}$ times = 1·314 times as much gas must enter the chambers as if the sulphur were burnt in the free state. This figure will permit a comparison of the results of the two processes.

The preceding calculations must be supplemented by some remarks. All practical men agree that a certain excess of oxygen is required, over and above the theoretical quantity, in order to promote and hasten the regeneration of nitric oxide to nitrous acid, &c. Bode ('Beiträge,' p. 15) assumes as a minimum 6 per cent. of free oxygen in the exit-gas of the chambers, and mentions that at 8 per cent. free oxygen his yield had been just as good, his consumption of nitre even a shade better than at 6 per cent. According to Hasenclever (Hofmann's Report, i. p. 370), in 1866, before Schwarzenberg, Gerstenhöfer had already calculated the theoretically best composition of burner-gas, but had only communicated it privately to several factories. His figures, which do not materially differ from Schwarzenberg's, are:—for brimstone,

10·65	per cent.	by volume of SO_2 ,	
10·35	"	"	O,
79·00	"	"	N;

for burning pyrites,

8·80	per cent.	by volume of SO_2 ,	
9·60	"	"	O,
81·60	"	"	N.

Scheurer-Kestner also assumes that the percentage of oxygen in the exit-gas = 6 per cent. He has, however, proved that the oxygen in the burner-gas is considerably less than according to the above calculation, probably owing to the formation of SO_3 (see below).

The above is certainly controverted by some. Vogt contends (Dingl. Journ. ccx. p. 105) that there ought to be only 3 or 4, never above 5 per cent. oxygen in the escaping chamber-gas;

beyond 5 per cent. he calls "very bad work." This opinion is not shared by other practical men. The other extreme is found at a large alkali-works, where it is believed that the best yield of sulphuric acid is obtained with 10 per cent. of oxygen in the exit-gas, certainly with a somewhat larger consumption of nitre than when 5 or 6 per cent. of oxygen is adhered to (4 per cent. of NaNO_3 upon the charge of sulphur, instead of 3 per cent.). The neighbouring works, burning the same pyrites under identical conditions, only allow 5 to 6 per cent. oxygen.

But if it is established that a certain excess of oxygen, although its presence increases the volume of gas, yet also increases the energy of the action in the chambers, it is, on the other hand, at least as well established that too great an excess of air greatly diminishes the yield and seriously increases the consumption of nitre. We here refer to the account of Olivier and Perret's first trials with pyrites (p. 244).

The upper limit of the excess of air has not yet been accurately defined; but 6.4 per cent. oxygen in the exit-gas, taken by Schwarzenberg as the basis of his calculations, must at any rate be considered very suitable for practical work. Accordingly a percentage of 8.59 SO_2 by volume in the burner-gas might be considered normal (Bode with 6 per cent. oxygen in the exit-gas arrives at 8.93 SO_2 in the burner-gas as a maximum), if this result were not modified by the formation of a certain quantity of SO_3 , as we shall see below.

For burner-gas from *zinc-blende* the following calculation has been transmitted to me by Mr. Hasenclever. Zinc-blende (in the pure state), ZnS , consists of 63 parts Zn + 32 parts S. For burning it into $\text{ZnO} + \text{SO}_2$, $3 \times 16 = 48$ parts O are required, for converting the SO_2 into SO_3 another 16 O; therefore for 95 ZnS , containing 32 S, altogether 64 O. This means that each kilogram S in zinc-blende requires 2 kilograms O, or 1398.7 litres at 0° and 760 millims., together with 5258.0 litres nitrogen = 6656 litres air. In order to make allowance for the 6.4 volume per cent. of oxygen required to be in excess in the exit-gas, we find this by the formula:—

$$n = \frac{6.4}{100} \left(5258 + \frac{100}{21} n \right),$$

$x =$	484.0	litres oxygen, corresponding to
	1820.7	„ nitrogen
	<hr/>	
	2304.7	„ air.

Consequently the normal gaseous mixture in roasting 1 kilog. blende consists of: .

699.4	litres SO_2 ,
349.7	„ O for forming SO_3 ,
484.0	„ O in excess,
5288.0	„ N entering with the theoretically necessary oxygen,
1820.7	„ N „ „ excess oxygen,
<hr/>	

8641.8 litres of gases.

This means that 100 volumes of the gas should contain :

8.12	vols. SO_2
9.69	„ O
82.19	„ N.

By an analogous calculation, published by Hasenclever in the 'Chem. Industrie,' 1884, p. 79, he arrives at exactly similar results.

So far, as we see from Hasenclever's calculation, theory would show that the strongest obtainable burner-gas from blende is not much inferior to that obtainable from pyrites (p. 312). But apart from the fact that here, as well as in the case of pyrites and to some extent even of brimstone, the theoretical figures are undoubtedly interfered with by the formation of sulphuric anhydride, there is, at least with all the older blende-furnaces, a far more potent reason why the practical percentage of SO_2 in blende-gases should be far below the theoretical one. Seeing that in those furnaces only $\frac{1}{2}$ or at most $\frac{2}{3}$ of the sulphur was liberated as SO_2 [and SO_3], that the other $\frac{1}{2}$ or $\frac{1}{3}$ remained behind in the state of ZnSO_4 , and that the nitrogen corresponding to the four atoms of oxygen contained in ZnSO_4 dilutes the burner-gas, it is easily understood why formerly it was considered *good* work if blende-gases contained 5 or at most 6 per cent. of SO_2 . The modern furnaces (p. 273 *et seq.*) undoubtedly yield better gases, not much inferior to the burner-gas from pyrites.

In the pyrites-burner, besides sulphurous acid, there is always *sulphuric anhydride* formed during the burning. This fact has

long been known, and was explained in 1852 by Woehler and Mahla, and again in 1856 by Plattner ('Die metallurgischen Röstprocesse') after many experiments, in this way—that many substances, one of which (ferric oxide) is present in large quantity in the pyrites-burner, dispose sulphurous acid to combine with the oxygen of the air to form sulphuric anhydride. We have already seen, and shall in the 15th Chapter see it in detail, that this reaction, which is most strongly exerted by finely divided platinum, can be used for the production of sulphuric anhydride itself. Another plausible explanation is, that in the cooler parts of the pyrites-burners sulphates of iron are formed, which at the hotter parts again split up into Fe_2O_3 and SO_3 . This explanation, however, is not sufficient for Fortmann's experiments (Dingl. Journ. clxxxvii. p. 155), according to which the whole of the fumes of anhydride appear the moment the pyrites take fire. Lastly, Scheurer-Kestner (Bull. Soc. Chim. 1875, xxiii. p. 437) explains the matter from the well-known fact that ferric oxide can act as an oxidizing agent by successively giving up and absorbing oxygen. None of these explanations fits exactly, especially because it is established that even on burning pure sulphur a little anhydride is formed (Fortmann, *loc. cit.*).

In Fortmann's experiments, made on a small scale, on burning pyrites far more SO_3 than SO_2 was formed, viz. in one experiment 4 times as much, in another as 5 : 3. Bode doubts whether Fortmann's results would hold good on the large scale, where the conditions are different and where the formation of such an enormous quantity of sulphuric anhydride would have been detected before. Scheurer-Kestner (*loc. cit.*) only found 2 or 3 per cent. of all the SO_2 converted into SO_3 , but a larger deficiency of oxygen in the gas than corresponds to this amount; and the later discussion between Bode (Dingl. Journ. ccxviii. p. 325) and Scheurer-Kestner (*ib.* ccxix. p. 512) has not cleared up the matter. In the last place, Scheurer-Kestner indirectly calculates from the oxygen that the sulphur of the pyrites is thus disposed of:—

As SO_2 in the burner-gas	65·5
„ SO_3 „ „	32·5
„ $\text{Fe}_2(\text{SO}_4)_3$ in the burnt ore	2·0
	<hr/>
	100·0

but he does not explain why, of the quantity of SO_3 calculated from the deficiency of oxygen, less than one tenth is actually found in the gas; and it thus seems to be established that this indirect calculation of the SO_3 from the oxygen contained in the burner-gas is inadmissible. Bode found afterwards (Dingl. Journ. ccxxv. p. 280) in three samples of gas from a shelf-burner:—

	a.	b.	c.	
Oxygen.....	11·80	10·65	11·94	p. c. by vol.
SO_2	6·20	6·35	6·55	„
N	82·00	83·00	81·55	„

To the N corresponds atmospheric oxygen

21·73	22·00	21·60
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Oxygen actually used for burning (if all Fe is burnt into Fe_2O_3):—

	a.	b.	c.	
For SO_2	6·20	6·35	6·55	p. c. by vol.
„ Fe_2O_3	2·32	2·38	2·46	„
Directly found as O.....	11·80	10·65	11·94	„
Total	20·32	19·38	20·95	„
Calculated.....	21·73	22·00	21·60	„
Therefore deficiency of oxygen	1·41	2·62	0·65	„

This latter quantity may have been used for forming SO_3 .

In order to decide the question of the formation of SO_3 on burning pyrites by more exact methods than those hitherto used, especially by Fortmann, I made, together with Salathe, a series of experiments (Deutsch. chem. Ges. Ber. x. p. 1824). It was found that SO_3 cannot, as Scheurer-Kestner had supposed, be absorbed and estimated by barium chloride, because even chemically pure SO_2 with BaCl_2 in the presence of O or atmospheric air at once gives a precipitate of BaSO_4 . Check tests proved that exact results were obtained by conducting the gas through an excess of standard iodine solution, retitrating the latter by sodium arsenite, and estimating the total sulphuric acid formed in another portion of the liquid by precipitation with BaCl_2 . By the retitration the quantity of SO_2 absorbed, by subtracting this from the total sulphuric acid that of the SO_3 was found. Two experiments with burning

Spanish cupreous pyrites, containing 48·62 per cent. of sulphur, in a glass tube in a current of air gave

	I.	II.
Sulphur obtained as SO_2	88·02	88·78 p. c.
„ „ SO_3	5·80	6·05 „
„ in the residue	3·43 } }	5·17 „
„ lost	2·75 }	

Of the sulphur of the burner-gas itself there were present

	I.	II.
As SO_2	93·83	93·63 p. c.
„ SO_3	6·17	6·37 „

Two other experiments were made in this way:—In the glass tube 50 grams of cinders from the same pyrites, in pieces of the size of a pea, were completely freed from sulphur by ignition, and fresh pyrites burnt as before, the gas passing through the cinders. Found:—

	III.	IV.
Sulphur as SO_2	79·25	76·90
„ SO_3	16·02	16·84
Residue and loss	4·73	6·26

Of the sulphur of the burner-gas itself there were present:—

	III.	IV.
As SO_2	83·18	82·00 p. c.
„ SO_3	16·82	18·00 „

On the large scale the formation of SO_3 will hardly be as much as in the last two experiments, because in the burners the gas passes through much less ignited ferric oxide than in our experiments.

By later experiments in my laboratory (*Chemiker-Zeitung*, 1883, p. 29) it was found that in roasting pyrites by itself 5·05 per cent., when passing the gases through a layer of red-hot pyrites-cinders 15·8 per cent. of the total sulphur reappeared as SO_3 , which entirely confirms the above results. On burning *brimstone* it was found that even here 2·48–2·80 per cent. of the sulphur was converted into SO_3 ; and this quantity was increased to 9·5–13·1 per cent. if the gases were passed through red-hot pyrites-cinders.

Further experiments were made by Scheurer-Kestner (Bull. Soc. Chim. xliii. p. 9, xlv. p. 98) with the gases from pyrites-kilns as given off in actual manufacturing. We quote here a series of his results, obtained with samples of burner-gas taken at various times—A, from a lump-burner, B, from a Malétra dust-burner.

	Volume per cent. of SO ₂ .	Sulphur converted into SO ₃ per cent. of total S. . . .	
A. <i>Lump-burner.</i>	7.3	2.8	Average 3.1
	7.5	5.8	
	6.5	1.2	
	6.6	1.0	
	8.3	0.0	
	9.9	2.8	
	6.2	8.4	
B. <i>Dust-burner.</i>	8.2	3.0	Average 3.5
	9.0	6.8	
	7.6	0.4	
	11.3	0.8	
	7.7	1.0	
	8.7	2.5	
	8.7	9.3	
	7.6	4.1	

The quantity of SO₃ formed is here found to be very irregular, varying from 0 to 9.3 per cent. of the SO₂; the average is decidedly less than in our laboratory experiments with pyrites.

F. Fischer (Dingl. Journ. cclviii. p. 28) has obtained the following results, which give at the same time an idea of the difference in the composition of the gases on the various shelves of a Malétra dust-burner:—

	SO ₂ per cent.	SO ₃ per cent.	O per cent.
A. <i>First test (shelf-burner).</i>			
Second shelf from below	0.96	0.44	18.4
Fourth „ „	1.52	0.68	16.6
Sixth „ „	3.81	0.97	12.5
Main flue	8.26	1.34	5.9
„ „	7.53	1.27	7.5

	SO ₂ per cent.	SO ₃ per cent.	O per cent.
B. <i>Second test</i> (shelf-burner).			
Sixth shelf from below	8.43	3.17	3.9
" " 	4.92	0.68	10.7
Second shelf from below	2.48	1.42	14.8
Fourth " " 	2.62	0.78	16.0
Main flue	5.80	0.65	10.6
C. <i>Lump-burner</i> up to	9.3	2.1	5.0

These tests were made by an expeditious method which cannot compete as to accuracy with that employed by me or by Scheurer-Kestner. The much larger quantity of SO₃ in proportion to SO₂ is perhaps explicable in this way.

If the burner-gases are not passed hot into a Glover tower, but are cooled in the old way, most of the SO₃ condenses in the shape of sulphuric acid, more than enough water for this purpose being contained in the air and the pyrites. Where the gases go into a Glover tower, this, of course, retains all the SO₃ previously formed, also in the shape of SO₄H₂ (Scheurer-Kestner, *loc. cit.*). We shall further on consider this fact in detail when speaking of the Glover tower and the formation of sulphuric acid generally.

The constant presence of sulphuric anhydride in various proportions in the burner-gas is, of course, a source of inaccuracy in the testing process according to Reich (see below), which indicates only the sulphur dioxide, as we shall see below; it causes, moreover, a deficiency of oxygen and an excess of nitrogen in the composition of the gases. Hitherto no satisfactory relation has been found between the amount of SO₂, SO₃, O, and N in the many analyses of burner-gases, as is apparent from the disputes between Scheurer-Kestner and Bode (*vide supra* p. 316; comp. also Ber. d. deutsch. Chem. Ges. vii. p. 1665), as well as from Fischer's tests just quoted.

Another source of dilution of the burner-gas, likewise not traceable quantitatively, is this—that the burnt ore does not contain pure Fe₂O₃, but sulphates of iron. Whether these are ferrous or ferric sulphate, they will always retain more oxygen than Fe₂O₃, and the nitrogen corresponding to this excess of oxygen must be found in the burner-gas. On the other hand, a little nitrogen will have to be deducted if in the burnt ore FeS is present; but this amounts to very little indeed.

Lastly, in the factories working with nitre decomposed immediately behind the burners, the dilution of gas caused thereby must be accounted for. The calculated density of NO_3H is 2.17823; we need only take this into account, as the NO_3H forms the largest portion of the gas given off by the nitre mixture. It differs so little from that of SO_2 (viz. 2.21126), that, looking at the small quantities in question, we can take the two as equal without any sensible error. Now in normal working order, and using a Gay-Lussac tower, certainly not above 5 per cent. of nitre on the burnt sulphur is consumed (corresponding to 3.7 per cent. of NO_3H), or 1.85 upon the SO_2 . Thus a gaseous mixture which, without the nitric acid, contains 8.59 per cent. of SO_2 , contains besides $\frac{1.85 \times 8.59}{100}$ nitric acid vapour, which increases its volume

to 100·1589, and diminishes the percentage of SO_2 in the total volume to 8·576—a diminution too slight to be traceable by analysis. Even if the nitric acid is not calculated as such, but as NO_2 or N_2O_5 , it has no sensible influence upon the analyses, even if the sample of gas is taken in a place where the nitrous vapours coming from the Gay-Lussac tower have already entered into the process.

Still all the above-mentioned causes concur in somewhat diminishing the percentage of SO_2 in the burner-gas; so that the figures stated by Schwarzenberg, viz.

11.23 per cent. by volume in burning sulphur,
8.59 " " " pyrites,

must be looked at as *maximum* figures, which in practice can only be approached, but hardly ever reached, and which never ought to be exceeded.

If the sulphurous acid in the burner-gas be estimated, this will sufficiently test the style of burning, since the oxygen of the gas must necessarily be in inverse proportion to its sulphurous acid—although not exactly, as the sulphuric anhydride comes into play. In practice, usually from 11 to 13 per cent. of oxygen is found in good burner-gas.

The innumerable observations made upon the percentage of burner-gas in chemical works during recent years have proved that with very good pyrites the above maximum figures can be very nearly approached, whilst with other ores, badly burning or containing unfavourable metallic sulphides, only 7 to 7½ per cent.

SO₂ in the burner-gas is attained (*e.g.* Büchner, Dingl. Journ. ccxv. p. 557). Of course, looking at the difficulty of keeping the evolution of gas exactly equal, the different observations made in the course of a day will frequently yield less than the above figures (*e.g.* Scheurer-Kestner, in Dingl. Journ. ccxix. p. 117, in one day found 6·5, 6·5, 6·0, 8·0, 9·0, 8·7; even greater differences occur in his tests quoted *supra*, p. 319); and they only signify the *average* percentage of the burner-gas. As a *minimum*, below which the gas of real pyrites ought never to fall, 6—as ordinary average, 7 to 8 per cent. SO₂ by volume can be assumed. If less is found, the draught should be cut off; if more, more air should be admitted.

All the above calculations only refer to pyrites proper—that is, containing only a few per cent. of other metallic sulphides. If the latter have to be roasted by themselves (for instance, preparatory to their metallurgical utilization), only poor gas can be obtained, partly because more sulphates remain in the residue, for which the corresponding nitrogen is found in the gas, partly because they must be roasted altogether with a larger excess of air.

According to Bode ('Gloverthurm,' p. 88), at Oker, poor ores with 27 per cent. sulphur, of which only 22 per cent. was combined with iron, the remainder being present as blende and barium sulphate, yielded gas with 5·5 per cent. SO₂. Lead-matt yields gas with 5 to 5·5 per cent.; coarse copper metal (with 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S), 5·5 per cent. SO₂.

According to Wunderlich (Zeitschr. f. d. chem. Grossgew. i. p. 74), the gas at Oker contains 5 to 7 per cent. SO₂; its temperature in the case of ores rich in sulphur reaches 360°, in the case of poorer ores about 230°.

Attention must be drawn to a circumstance frequently overlooked—that for technical purposes very rarely a reduction of the volumes of gases to 0° and 760 mm. is effected. This matters less in ordinary gas-analysis than in tests like that of Reich, where the gases are compared with a fixed quantity of SO₂ assumed to be at 0° and 760 mm. This causes most tests made by Reich's method to indicate less than the real percentage of SO₂ present.

Usually 4 per cent. SO₂ in the gases entering the chambers is considered the minimum at which it is possible to make sulphuric acid without actually losing money by the process. Locally, of course, this may be modified to some little extent. At

Freiberg 4 to 3½ per cent. SO_2 is stated as the minimum at which the sulphuric acid can be carried on without pecuniary loss. The average at those works, where a great variety of poor ores, all arsenical, and "matt" is roasted, preparatory to the smelting processes, is from 5 to 7 per cent. SO_2 in the burner-gas.

Comparison of Brimstone and Pyrites as Material for Sulphuric-acid-making.

We have seen above that the burner-gas from brimstone is richer than that from pyrites in the proportion of 1 to 1.314; that is to say, under equal conditions, the gas generated in burning pyrites occupies 1.314 times as much space as if the same quantity of sulphur had been employed as brimstone. From this it directly follows that the gas will also require as much more chamber-space; thus, for an equal production of sulphuric acid, the chambers must be about one third larger if working with pyrites than if working with brimstone. Usually it is assumed that the consumption of nitre has to be increased in a similar ratio; this, however, is not the case, as a properly constructed Gay-Lussac tower retains almost the whole of the nitre-gas, and the excess volume of air is not of great importance. Now-a-days, indeed, in well-managed works, less nitre is used with pyrites than has ever been used with brimstone.

Leaving the nitre out of consideration, the advantages of using brimstone are:—a somewhat higher yield of acid (see Chap. XIII.); rather less cost of plant, and less trouble with the burners if any thing goes wrong; and, above all, much greater purity of the sulphuric acid, especially from iron and arsenic (though this is important only for sale acid). If brimstone could be had at the same price as the sulphur in pyrites, nobody would hesitate for a moment to employ the former; and even a moderately higher price would not deter from this; but where the pyrites-sulphur, as is the case in most industrial countries, only costs one half or even a quarter of the price of brimstone, the latter can no longer be employed, except for *pure* acid; and even this, when the difference in price is very large, can be more cheaply made from pyrites than from brimstone.

Owing to this cause, the manufacture of brimstone-acid in Europe is confined to small factories which make specially pure

acid for bleach-works &c. A somewhat considerable number of such factories are still existant in England, whilst very few are found in other European countries.

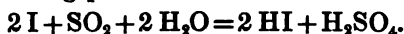
In America until quite recently all sulphuric acid was made from Sicilian brimstone; but the notes given above (p. 48) as to the consumption of pyrites in America show that this is rapidly gaining ground.

It is frequently asserted that sulphuric-acid chambers worked with brimstone last very much longer (up to three times) than with pyrites. It is not impossible that there is *some* difference in this respect, especially in the case of pyrites containing much arsenic; but even this is not certain, and at all events the difference in the duration of the chambers is nothing like so great as was formerly believed, and forms no item in a comparison of costs (comp. Chap. VI.).

The Quantitative Estimation of Sulphurous Acid in the Burner-gas.

This has been hitherto nearly always effected by Reich's process, which consists in aspirating the gas through a measured quantity of a solution of iodine, to which a little starch has been added. This is carried on till the blue colour of the solution disappears; the amount of gas aspirated in proportion to the constant quantity of iodine employed admits of calculating the percentage of SO₂ in the gas.

The reaction taking place is as follows :



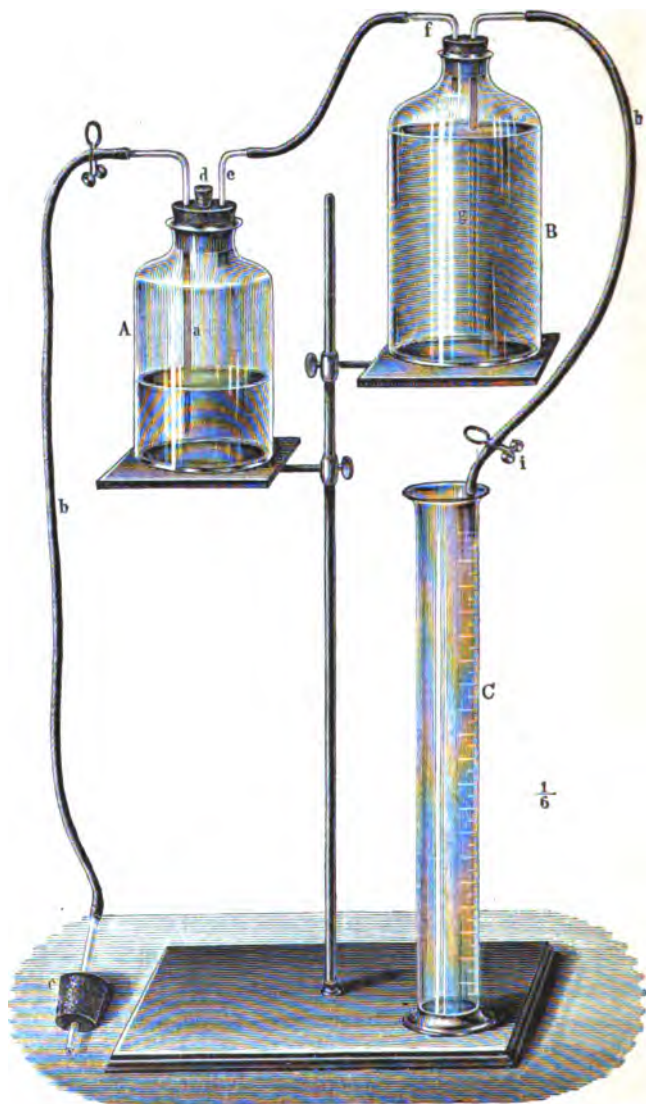
The operation is carried on with the apparatus shown in fig. 99. A is a wide-mouthed bottle of about 200 or 300 c.c. capacity, provided with a three-times perforated india-rubber cork. Through one perforation passes the glass tube *a*, which, by means of the elastic tube *b*, serves for introducing the gas; for this purpose a hole is drilled in some convenient part of the burner-pipe, and the india-rubber cork *c* exactly fitted into it. The second, somewhat wider perforation is closed by the small plug *d*; through the third the elbow tube *e* passes, which is connected with the corresponding tube *f* of the bottle B, holding 2 or 3 litres. The latter serves as an aspirator—the glass tube *g*, reaching to its bottom, being continued into an elastic tube *h*, closed by the pinchcock *i*, the whole when once filled serving as a siphon. The graduated cylinder, C, holds 250 cub. centims.

When the sulphur dioxide in any gaseous mixture has to be estimated, the cork *c* is inserted into a hole of the pipe conveying the gas.

The vessel *A* is filled up to about half of its capacity, through *d*, with water; and *B* is filled almost entirely. A small quantity (usually 10 c.c.) of standard iodine solution (12.65 gram *I* in 1 litre of water) is added to the water in *A*, along with a little starch, by which the water assumes an intensely blue colour. The pinchcock on the elastic tube *b* is shut so that no air can enter into *A*; *i* is opened, so that water runs out until the air in *A* and *B* is so far expanded that the column of water in *B* is supported. The water then ceases to run, provided that everything closes air-tight; if not, the water will continue to run. When the apparatus has been thus tested, *i* is shut and *b* opened; then *i* is opened so that the water runs out slowly, the gas to be tested entering through *a* in single bubbles and rising through the coloured water. As soon as the SO_2 contained in it gets into the water, it converts the free iodine into iodhydric acid; and after a certain time the liquid will be decolorized, which at last happens very suddenly and can be very accurately observed. As soon as this happens, the cock *i* is closed. By this preliminary operation the whole of the inlet-tube is filled with the gas to be tested.

Now *d* is opened, and a measured volume (say, *n* cub. centims.) of standard iodine solution is put into the vessel *A*, by which, of course, a blue colour is again produced; *d* is closed again; *i* is cautiously opened, and water is run out till the liquid in *a*, which, on opening *d*, had risen to the level of the outer liquid, has been depressed to the point of the tube, in order to expand the gas in *A* up to the degree of pressure at which the following observation takes place; then *i* is quickly shut, all the water that runs out is poured away, and the empty graduated vessel *C* is put back into its place. Now *i* is opened, and, by the running-out of the water, gas is slowly aspirated through *A*, till the liquid is decolorized again, whereupon *i* is closed, and the volume of the water run out into the graduated cylinder is measured. We will call it *m* cub. centims. In this process no sulphurous acid escapes unabsorbed, if the bottle *A* is constantly shaken; it is best to do this with one hand, holding open the pinch-cock *i* with the other hand, and letting this go the moment the colour has vanished, or even when it is but faint, as it generally goes away on shaking a little longer.

Fig. 90.



It is advisable to add to the iodine solution a little sodium bi-carbonate, which will facilitate the absorption of SO_2 (Cl. Winkler).
If a second testing is to be made, without any further alteration

a fresh quantity of iodine solution can be put in, and the process recommenced. When this has been repeated a few times, the decolorized liquid in A, after a short time, again turns blue of itself, because then its percentage of HI has become so large that it decomposes on standing and liberates iodine. This liquid must then be poured away, and replaced by fresh water and a little starch solution.

The calculation of the result is as follows :—The n cub. centims. of iodine solution, provided it contains 12.65 grams per litre, by its decolorization shows 0.0032 gram SO_2 , which, at 0°C . and a barometrical pressure of 760 millims., occupies a volume of $1.114 \times n$ cub. centims. If the barometer shows b millims., and the thermometer $t^\circ \text{C}$., and the difference of water-levels in the aspirator is $=h$ millims., equal to $\frac{h}{13.6}$ millims. of mercury, the exact volume of $0.0032 \times n$ gram SO_2 is

$$1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665 t) \text{ cub. centims.}$$

As the water run out, and thus also the gas aspirated through A, amounts to m cub. centims., the volume of the aspirated gaseous mixture, before the absorption of the SO_2 contained therein, must have been

$$m + 1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665 t) \text{ cub. centims.,}$$

and the percentage of SO_2 in volumes of the gaseous mixture

$$\frac{100 \times 1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665 t)}{m + 1.114 \times n \times \frac{760}{b - \frac{h}{13.6}} \times (1 + 0.003665 t)}.$$

In many cases a correction for the barometrical and thermometrical changes will not be required ; and the formula is then simply

$$\frac{111.4 \times n}{m + 1.114 \times n} \text{ per cent. } \text{SO}_2.$$

If the percentage of SO_2 in the gas is very small, and thus m very large in proportion to n , the formula may be simplified into

$$\frac{111.4 \times n}{m}$$

If 10 cub. centims. of a decinormal iodine solution (= 12.65 grams in 1000 cub. centims.) have been put into A, this quantity, according to the above-given formula, will correspond to 0.032 gram, or 11.14 cub. centims. SO_2 , at 0°C . and 760 millims.; and this number need only be multiplied by 100, and divided by the number of cub. centims. of water collected in C, *plus* 11, in order to find the percentage of SO_2 in the gas. The barometrical and thermometrical corrections are in this case, of course, neglected. The following Table will save this calculation. On employing 10 cub. centims. of decinormal iodine solution, the following number of cub. centims. collected in the graduated cylinder, C, show:—

cub. centims.	Volume percentage of SO_2 .
82	12.0
86	11.5
90	11.0
95	10.5
100	10.0
106	9.5
113	9.0
120	8.5
128	8.0
138	7.5
148	7.0
160	6.5
175	6.0
192	5.5
212	5.0

Even if the gas to be examined is taken at a point where it is already mixed with nitre gas, this will not exercise any practically important influence upon the result. We have already seen that, in ordinary work, for each 100 parts of SO_2 only 1.85 NHO_3 , or its equivalent as N_2O_3 or NO_2 , exists in the gas. In such dilute aqueous solutions as come into question here nitric acid hardly at all oxidizes sulphurous acid; this, however, is done by nitrous and hyponitric acids. Even if we assume that only NO_2 is formed

(which is going much too far), this could at most oxidize its equivalent in SO_2 , according to the formula



46 NO_2 thus oxidizes 64 SO_2 , or 1.35 NO_2 (the equivalent of 1.85 NO_2H) only 1.88 SO_2 ; in other words, in the worst case, never happening in practical work, of 100 parts SO_2 1.88 part would be oxidized by nitrogen acids instead of iodine. Even this maximum error would, say, at 10 per cent., only amount to a deficiency of 0.188 per cent.; but this is certainly reckoning it much too high.

Lunge's Test for total Acids in the Burner-gas.

Considering the inaccuracy inherent in Reich's test, owing to the constant presence of sulphuric anhydride in the burner-gas (comp. *supra*, p. 315 *et seq.*), the question arises whether it would not be better to substitute for it a test showing the *total acidity* of the burner-gases. There is no difficulty in doing this, either by the method indicated for testing the exit-gases, or in a more expeditious way by employing in the apparatus, fig. 99, a caustic-soda solution tinged red by phenolphthalein (litmus is not applicable in this case, nor is methyl orange, which acts differently upon sulphurous and sulphuric acid, comp. p. 165). I have shown this method to be quite practicable and accurate, and it is already carried out at several works for the regular control of the process. A decinormal solution of caustic soda is employed, of which 10 c. c. are tinged red with phenolphthalein and diluted to about 100 or 200 c. c. The gas is aspirated through it slowly, exactly as in Reich's test, with continuous shaking. Especially towards the end the shaking must be continued for a while (say $\frac{1}{2}$ minute) each time after aspirating a few c. c. of gas through the liquid, till the colour has been completely discharged, which is best ascertained by putting a white piece of paper or the like underneath the bottle. The calculation is made exactly as with the iodine test, counting all the acids as SO_2 . A large number of practical tests made in this manner have shown that the percentage of total acids calculated as SO_2 is always larger than the figures found by the iodine test owing to the presence of SO_3 , and that the results of the former test agree with those of gravimetical estimations.

The absorption-bottle used by me differs from Reich's in

having an inlet-tube for the gas, closed at the bottom, and perforated with many pin-holes, through which the gas rises in many minute bubbles, instead of one large bubble, as shown in fig. 100. Experience proves this to be greatly superior to fig. 99.

Fig. 100.



Estimation of Oxygen in Burner- and Chamber-gases.

Although burner-gas is not generally tested for oxygen, this test being reserved for the exit-gases, we will in this place describe the methods employed for estimating oxygen in any of the gases occurring in the manufacture of sulphuric acid.

Oxygen is for technical purposes always estimated by means of an absorbent, observing the contraction of volume produced. Some of these absorbents are not employed now, as nitric oxide (used by Priestley and recently by Scheurer-Kestner, *Compt. rend.* lxxviii. p. 608; also lately recommended by Wanklyn), ferrous hydrate (Vogt, *Dingl. Journ.* ccx. p. 103), and others. Cuprous chloride, in ammoniacal or acid solutions, may be employed for absorbing oxygen, but it has no advantages over pyrogallol or phosphorus, and several drawbacks, so that it cannot be recommended. The choice really lies between the two agents just mentioned.

Of these *pyrogallol* must be used in an alkaline solution, and it acts very promptly indeed. Its use for this purpose was proposed by Chevreul as early as 1820, but it became general only through Liebig many years after. It is true that this reagent in the presence of pure oxygen forms some carbon monoxide (Crace Calvert, Proc. Manch. Lit. and Phil. Soc. 1863, p. 184); but this never happens with gaseous mixtures containing no more oxygen than atmospheric air (Poleck, Zeitschr. f. analyt. Chemie, 1869, p. 451). It is therefore altogether reliable in the present case, and is very much employed. Its drawback is that the solution (25 grm. potassium hydrate and 10 grm. pyrogallol to 400 c. c. water) gradually thickens and becomes useless long before this somewhat expensive reagent has been used up.

Phosphorus is one of the oldest absorbents for oxygen, and it has come into use again, as the manner of employing it has been properly studied, and since it is found in trade in very thin sticks, offering a great surface. Of course it must be kept under water, and must be exposed only to the gas to be analyzed. It acts only at a temperature of at least 16° , better a little above; this is the first condition to be observed in its use, but it is easy to attain if the apparatus is kept in a somewhat warm place (near an acid-chamber). The action of phosphorus on oxygen is interfered with by traces of tarry matters and the like; but such do not occur in chamber-gas. As it is, the gases, both for the pyrogallol and the phosphorus test, are often previously washed and freed from acids by passing them through a solution of caustic potash; but there is generally no great error made by omitting this treatment. The action of the oxygen on the phosphorus is at once indicated by the formation of a white cloud, and it is necessary to wait a few minutes till that cloud has completely disappeared, when the absorption of oxygen will be complete. Once charged, such an apparatus may serve for hundreds of tests, but it should be kept from daylight.

The apparatus employed for estimating oxygen in gaseous mixtures may be of various descriptions. Those most used are Orsat's apparatus (comp. Lunge and Hurter's Alkali-Makers' Pocket-Book, p. 74, and Winkler-Lunge's Technical Gas Analysis, p. 47), Lindemann's apparatus (ibid. p. 51), and M. Liebig's apparatus (Dingl. Journ. ccvii. p. 37, and ccxxxiii. p. 396; to be obtained from H. Geissler, Bonn); Younger's apparatus (J. Soc. Chem. Ind.

1887, p. 348) is a slight modification of the latter. The two former can be used for phosphorus or pyrogallol, the latter for pyrogallol only.

Of course Hempel's, Bunte's, or any other apparatus for general technical gas analysis may be employed as well.

Instead of taking only single samples of the escaping gas, it is advisable, along with these, to collect an average sample (say, for 24 hours) by aspirating a certain quantity (say, about 50 litres) by means of a large aspirator with the outlet-cock very slightly opened. Owing to the slowness of the aspiration, the gas standing over the water in the aspirator will be thoroughly mixed up, and by taking a sample from the aspirator the *average* percentage of oxygen can be estimated with some degree of accuracy. We shall treat this matter more in detail in the 7th Chapter, when describing the testing of the exit-gases.

Estimation of the Oxides and Acids of Nitrogen in Gaseous Mixtures.

Burner-gas will contain the above acids, if the "potting" has been done either within or close to the burners, as is usual in England. The acids and oxides of nitrogen are, however, but exceptionally estimated in burner-gas, and not very often even in chamber-gas; the latter is not indispensable, because the colour of the chamber-gas on the one hand, and the testing of the "drops" on the other, which we shall describe in the 7th Chapter, are sufficient for guiding the manufacturer in his work.

In well-conducted works, however, the chamber-exits are tested not merely for total acidity, but also for nitrogen acids separately. For this purpose the prescriptions formulated in 1878 by the British Alkali-Makers' Association may be observed, which we shall give in detail later on (Chap. VII.). These do not extend to nitric oxide, but we shall see that it is easy to estimate this at the same time. In this place we shall give a short outline of the methods employed by Lunge and Naef for their extended experimental investigation of the vitriol-chamber process (*Chemische Industrie*, 1884, p. 5) for *estimating nitrogen oxides and sulphur dioxide at the same time*. The pipe bringing the gas from the chambers is continued into a Y-pipe, both branches of which are connected with sets of absorbing-tubes. One branch is connected

with three U-tubes containing concentrated pure sulphuric acid (for retaining N_2O_3 and N_2O_4) and a fourth tube containing an acidulated solution of potassium permanganate (for retaining NO). The other branch of the Y-pipe first leads into a long glass tube filled with cotton wool or glass wool, where any drops of mechanically carried-over sulphuric acid are retained, and then into two U-tubes containing pure caustic-soda solution (for estimating SO_2). At the end of both sets of tubes there is an aspirator, consisting of a large glass bottle, holding about 20 litres, divided into single litres, with a tap or tap-siphon leading into a similar bottle, so that the quantity of water run out is a measure for the quantity of gas passed through each set of tubes. The gas remaining in the aspirators is tested for *oxygen* by absorption; *nitrogen* by difference. *Sulphur dioxide* is found by oxidizing the caustic-soda solution with bromine-water and precipitating the sulphuric acid formed by barium chloride. In the sulphuric acid *nitrogen trioxide* and *tetroxide* are estimated in the way indicated in Chapter III. (p. 177 *et seq.*), by testing both with permanganate and with the nitrometer. The tube filled with potassium permanganate must have retained the *nitric oxide*, which is found by adding titrated ferrous sulphate solution and re-titrating with permanganate. Where the quantity of SO_2 in the gas is considerable, this method cannot be employed; in this case it is not possible to separate the N_2O_3 and N_2O_4 , and the method otherwise used for the chamber-exits must be employed (Chapter VII.).

We purposely abstain from giving any methods for estimating *nitrous oxide*, N_2O , in gaseous mixtures, as all those hitherto proposed are utterly fallacious for discovering or estimating the small quantities of N_2O *possibly* occurring in the vitriol process, in the presence of so many other gases.

CHAPTER VI.

CONSTRUCTION OF THE LEAD CHAMBERS.

WE have already seen, in our historical survey, through how many stages the construction of that apparatus has gone in which now-a-days all sulphuric acid, except the Nordhausen oil of vitriol, is made, viz. the *lead chamber*. The reader already knows that sulphuric acid is formed by the oxygen of the air being transferred to sulphur dioxide through the intervention of the acids of nitrogen and with the aid of a molecule of water, thus :



All the substances entering into the process are in the state of a gas or (as the water) of a vapour. The reaction takes a certain time, as the nitrogen compounds which serve as carriers of oxygen have to be frequently reduced and reoxidized, and as the gases and liquids are only gradually mixed so intimately that they can actually enter into reaction. There must therefore be a space provided in which large quantities of gas can remain for some time. According to the calculations given on pp. 308 and 311, for each kilogram of sulphur in the state of brimstone 6199, or in the state of pyrites 8145 litres of gas, reduced to 0° and 760 millims. pressure, must enter into reaction ; and these figures are a good deal increased by the higher temperature, the steam, &c. In order to harbour such very large quantities of gas, very large spaces must be provided. Since the strongest acids have to be dealt with, both in the liquid and the gaseous form, most materials otherwise used in building are out of the question ; and since, of those suitable, glass, earthenware, &c. are excluded by the large size of the apparatus, practically only *one* material remains which is sufficiently cheap and suitable for the purpose, viz. *lead*. The disadvantages of this metal, such as its great weight, its softness

and lack of rigidity, its easy fusibility, its comparatively high price, cannot outweigh the advantages which none of the base metals shares with it for our purpose, viz.:—its great chemical resistance to the acid gases and liquids; its ductility, which permits rolling it into large sheets; its extraordinary pliability and toughness, by the assistance of which it can easily be shaped in every possible way; and, lastly, even its easy fusibility, which permits the edges of two sheets to be so completely united by melting together with a strip of lead, that they form a whole for all practical purposes, so that it is possible to make vessels of indefinitely large size and any shape, provided that care be taken to support the walls of the vessel on the outside, lest they collapse by their own weight.

A special advantage of lead is this, that even after a number of years, when the chambers have become quite worn out, the greater portion of its value can be recovered by remelting the material; even the mud containing lead can be utilized.

The attempts to make sulphuric-acid chambers from other materials than lead have completely failed. To this class belongs the proposal of Leyland and Deacon (patents of September 10th and December 2nd, 1853) to make them of *hard-burnt firebricks*, slate, sandstone, basalt, &c., set with a mixture of melted sulphur and sand. *Vulcanized india-rubber* or *gutta percha* are just as useless; Krafft (Wagner's 'Jahresb.' 1859, p. 137) found that gutta percha in an acid-chamber loses six times as much weight as lead, and half as much again of its surface. It would be absolutely impossible to use it, because it softens at the temperature of the chambers, and in that state is even more easily acted upon by the gases. Simon's *zeiodelite* (Dingler's 'Journal,' clv. p. 100), a mixture of 19 sulphur with 42 pounded glass, to be employed in slabs of $\frac{1}{2}$ inch thickness, has, no doubt, never been so much as tried for this purpose, no more than the *sheets of glass* proposed by Wilson and others.

We will now describe the *erection of lead chambers*.

The chambers are always placed at some elevation above the ground-level. Now-a-days, probably, chambers are nowhere found placed on the ground itself, or on such low foundations that one cannot at least walk about underneath; mostly their bottoms are much higher than this. The first object of this is to give the opportunity of ascertaining whether the chambers are tight. If

their bottoms are not easily accessible, large quantities of sulphuric acid may get lost in the ground before any loss is detected. And this not merely means a loss of the acid, but still more: the foundations are corroded and undermined; and the whole structure may collapse. The expense of building the chambers on pillars &c. is not thrown away, as the whole space underneath can be used as a warehouse which in winter time has always a moderately high temperature; or it may even, if high enough, be utilized for the pyrites-kilns &c. In the latter case it should be from 17 to 20 feet high. At some works, which are pressed for space, even the saltcake-furnaces, ball-furnaces, &c. are built underneath the chambers; but the space below them in this case must be at least 30 feet high.

In any case the soil must first be examined to ascertain whether it affords a safe *foundation*; for if it settles more in one place than in another, the chamber gets out of plumb, and its bottom out of level, which, owing to the acid lying on the latter and on the instability of the chamber-sides, causes great inconvenience. A rocky or pebbly ground is best; next to this, sand or clay; marl or limestone are bad, because sometimes acid will run over accidentally, which acts upon it; and this may happen even with clayey soil. In such cases the whole soil underneath the chambers must be protected by a layer of asphalte.

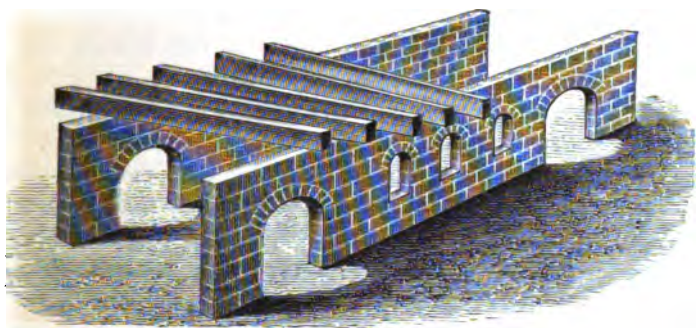
The pillars upon which the chamber is erected must, of course, go down to the "rock," as in any ordinary higher building. If the accumulation of made ground or loose earth is so deep that it would be too costly to excavate and raise the pillars from below, piles must be driven in, according to well-known building-rules, and the pillars built upon these.

The pillars themselves can be made of brickwork, stone, cast iron, or wood. Sometimes, instead of single pillars, two longitudinal walls are erected, connected by cross joists and interrupted by doors, windows, &c., as shown in the sketch, fig. 101 (p. 337). Such long walls take much material and make the room underneath the chambers dark, in spite of the windows. They are only suitable where the chambers are placed unusually high in order to build furnaces underneath. Up to a height of about 26 feet metal pillars seem preferable.

The cheapest pillars are those made of wood or bricks; very rarely they are made of stone—much more frequently of the dearer

but much stronger and more durable material, cast-iron. If made of wood, round or canted balks of at least 10 inches (better 12 inches) thickness must be employed. Mostly fir or pine wood is

Fig. 101.



used, especially Scotch fir; but the American pitch-pine or yellow pine, such as is used for ship-building, is preferable (on account of its much greater durability) in spite of its higher price. This applies not merely to the foundation pillars, but even more to the frame of the chamber itself. The pillars must vary in their thickness, mutual distance, and manner of being stayed, according to their height and the weight resting upon them (which may be taken at 150 lbs. per superficial foot of the total chamber-area, for the lead, timber, and acid, the latter alone in a full chamber amounting to 120 lbs. per superficial foot); but for an average height of 10 to 13 feet, which will not often be exceeded with wooden pillars, they ought not to be further apart than 10 to at most 13 feet from centre to centre. In any case they are put into a stone socket projecting from the ground, lest the bottom of the pillar be damaged by any moisture or acid; the stone has at the top a hollow of $\frac{1}{2}$ to 1 inch depth, into which the foot of the pillar fits exactly; at first a little tar is poured into it. Wooden pillars do not last for ever; they are not to be trusted very much, and are rarely found now in larger works, at any rate as principal pillars, except where wood is very cheap.

Much more frequently *brick pillars* are employed. These also are not often made above 13 feet, at most 15 feet high; they are at least 18 inches (better 2 feet) square. They are made of common

bricks with a mortar very poor in lime. The mortar can be made very cheaply and of excellent quality in this manner:—A ton of alkali (tank) waste, two tons of furnace-cinders, 6 to 8 cwt. of slaked lime, and sufficient water are ground up in a pug-mill, till the mixture has become a homogeneous tough mass of the consistency of putty. This usually takes an hour. Instead of lime slaked on purpose, the lime riddlings from the bleaching-powder manufacture, which are otherwise worthless, can be used, and with equally good results. This mortar is used without any sand; it can be kept for some days, and sets very quickly and hard, much more so than ordinary mortar, and is even more resistant to acids. Thus from worthless materials, which otherwise cost some expense for their removal, a mortar of much greater value than lime mortar can be made, which, of course, can be used for any other purpose as well; its only drawback is that the joints are not white, but blackish grey, and that salts effloresce on the surface, which, however, after having been washed away a few times, do not return again. Undoubtedly the great hardness of this mortar is owing to the presence of sulphate of lime, similar to Scott's selenite mortar.

The brick pillars in many works have been replaced by cast-iron ones, because they are not very durable, especially at the top, where the beams rest. Even the bricks themselves become rotten by contact with the acid, and only stand better if previously soaked in hot tar; but they take the mortar very badly after that. They may also be painted with hot tar afterwards.

On the continent, where in consequence of the colder winters and hotter summers the chambers have to be placed in a closed building, the pillars may be built in a piece with the main walls of this building; but it is even then best to keep them to themselves, as their settlement is different from that of the main walls.

Chambers 20 feet and upwards in width are sometimes built with mixed pillars—viz. brick pillars for the two long sides, and wooden pillars for the centre row.

Stone pillars are not often used for acid-chambers. Made of rough stones, they would be extremely clumsy; and hewn stone in most places is too dear. On the other hand, of course, stone pillars of the latter kind are very substantial, and last almost for ever, unless the stone be very soft and rotten.

In the larger works in England *cast-iron* pillars have latterly been almost exclusively employed, in spite of their higher cost. These

can be made 30 or even 36 feet high; they take very little space, and are almost imperishable if painted from time to time. They can be weighted a good deal more than any other pillars, unless these are made very thick; and they can be used as supports for many other purposes by means of cast-on brackets or even of pieces bolted on subsequently. A brick or stone foundation must be made for them up to the level of the ground or a little higher; the top stone is made with a socket to receive the foot of the pillar, as in the case of wooden ones; or holes are drilled into the stone, corresponding to other holes in the base of the column; and the joint is made by iron cramps, fastened by pouring in melted lead, or in some other way.

The cast metal columns are now frequently made of an H-shaped section, and a little tapering upwards. Fig. 102 will show this more distinctly, together with a bracket on each side for receiving a wooden stay for the timber above. Another, cross-shaped section is shown in fig. 103. These constructions are better adapted for brackets, &c. than round columns. If higher than shown in the figures (15 feet), they must be correspondingly stronger—for instance, for 20 or 24 feet height, 12 inches diameter at the base. Such columns can be placed at 20 feet distance from centre to centre, if the beams resting upon them are strong enough.

Sometimes the columns are made of wrought iron, of the section shown in

Fig. 102.

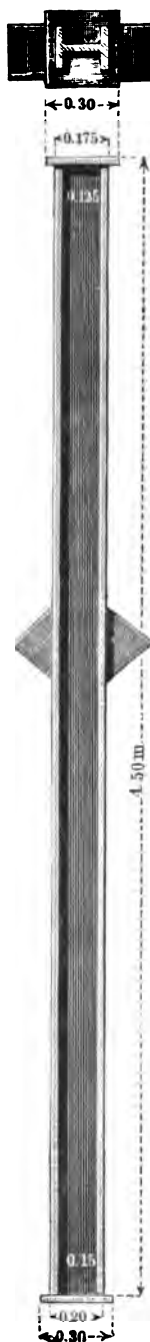


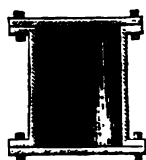
Fig. 103.



fig. 104. They are a little dearer than cast-iron columns, but more durable and reliable.

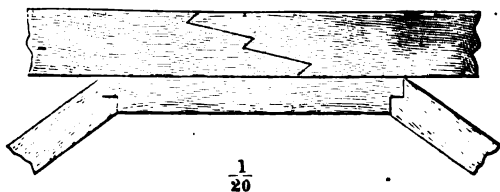
The pillars are in most works placed so that they stand directly under the side frame, which has to carry the weight of the chamber sides, and in the English system also the whole weight of the chamber top. This, however, in any case suffices only for very narrow chambers; for chambers of ordinary width (from 20 feet upwards) a centre row of pillars must be added to prevent sagging of the joints. But as the weight of the acid in a full chamber may be up to four times as much as that of the frame and lead combined, it seems more rational to place the pillars more inside, in which case two rows suffice even for a chamber of ordinary width.

Fig. 104.



Above the pillars there are generally, in England, *longitudinal sleepers*. If there is a continuous wall in the place of pillars, to cover this with a 2-inch plank will be sufficient; but if there are separate pillars, the sleepers must be strong enough to support the whole structure of the chambers, both wood and lead; and their strength will then depend on the distance between the pillars. With chambers of 20 feet height, and distances between the pillars of 20 feet from centre to centre, the longitudinal sleepers ought not to be less than 12 to 14 inches high, and ought, besides, to be supported by stays, as shown in fig. 105. With the pillars at shorter distances (say 10 or 13 feet), timber of 9 by 12 inches, always on edge, suffices for the longitudinal sleepers. The joints of the beams of which they consist ought to be well connected, as shown in fig. 105, and ought to be placed between the pillars, where they

Fig. 105.



are supported from below by the stays. The upper face of the sleepers must be as well levelled as possible from one end of the chambers to the other. Above these the *cross joists* are placed, running from side to side, and made long enough to carry the side

frames, and to leave, moreover, a passage round the chambers. For the latter object only every third or fourth joist need project about 5 feet on each side. On the Continent the joists are usually made square in section, in England always of planks on edge, which seems preferable, because for an equal volume of wood the support of the chamber-floor is divided over a larger area, and the erection is thus strengthened. Here also the span must be considered in fixing the strength of the wood. If chambers are much less than 20 feet wide, which rarely happens now, no centre longitudinal sleeper is needed, and the cross joists should have 9 by 3 inches section, and corresponding length. Wider chambers require a centre row of pillars and sleepers; and in this case, as such long planks are not easy to get, the joists can be made in two lengths, resting on a side and on the centre sleeper. The horizontal distance of the floor-joists is usually 12 inches from centre to centre. Some works have them 3 by 11 inches. The length of the joists is equal to the width of the chambers *plus* the chamber-frame, *plus* the width of the passage.

The joists are covered with a 1-inch floor, laid quite level in all directions. As the flooring-boards might easily warp afterwards from the heat of the chambers, this must be prevented by the well-known methods of carpentry. The edges of the boards are planed so as to form a perfectly smooth floor without any chinks.

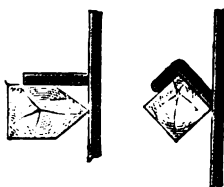
Another system of building is more in favour on the Continent. First, from pillar to pillar strong sleepers are laid across the width of the chamber; upon these a large number of longitudinal joists are laid, and the flooring-boards on the top of these, running from one side of the chamber to the other.

Upon the whole the *frame of the chamber* is erected, which serves for supporting the lead. It consists, for each side of the chamber, of a sole-tree and a crown-tree, connected by uprights, and further tied by cross rails or stays. The sole- and crown-trees and uprights are either of square section (say 6 inches square for a chamber up to 20 feet high) or oblong (say 7 by 3 inches). The sole- and crown-trees lie on the flat side; and the uprights are mortised into them so that their longer side just covers the trees. In the corners the trees project over and are rabbeted into each other. If no cross rails are employed, the uprights are placed 3 feet 3 inches apart from each other; if they are connected by cross rails, they can be placed 4 feet apart. The cross rails are

3 inches by 2 inches; they are only partly let into the uprights, in order not to weaken these; and are placed at vertical distances of 4 to 5 feet from each other. The chamber-lead is kept a little away from the woodwork in order to expose the lead always to the cooling-action of the air. If this is not done, the lead is found to be quickly corroded in the parts protected against radiation of heat by the wood; it has even been observed that insects from the wood have bored through it. It is more and more coming into fashion to shape the woodwork so as to present the least possible contact with the lead, as shown in figs. 106 and 107. Almost the

Fig. 106.

Fig. 107.



same effect is obtained by using round timber for uprights.

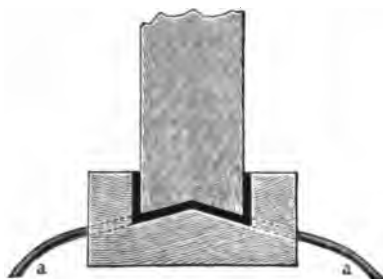
The best kind of timber for this purpose, as well as for all others where acids are concerned, is American yellow-pine or pitch-pine; but as this is frequently too expensive, ordinary red-wood is also very much in use. It is useful to protect it against the action of the acids by a coating of whitewash, which is at the same time a slight protection against the risk of fire. Another kind of protection from the former, although not from the latter, risk consists in painting the woodwork with coal-tar, or preferably with a sort of tar-varnish, made by dissolving coal-tar pitch in heavy tar-oils, and known as "prepared" or "refined" tar (Lunge's 'Coal-Tar and Ammonia,' 2nd edition, p. 277). The latter enters better into all the pores of wood and on drying does not leave so many crevices; it is altogether preferable to raw coal-tar for painting wood, iron, or brickwork, and is not much dearer.

The painting of the woodwork is best done twice over, and before the lead is put on, so that all parts can be reached by the brush.

Special care must be taken lest any acid should get into the mortise-holes, where the uprights are joined to the sole-trees, &c. No empty space should be left here where any acid could lodge, but all points should be filled up with coal-tar pitch or the like. It seems also another good plan to cut out the bottom of the

upright, and make it fit on to a corresponding saddle-shaped part of the sole-tree, as seen in fig. 108. Two small lead pipes drain

Fig. 108.



away any liquid collecting in the low corners, so that no acid can ever lodge there and cause the wood to decay.

In France sometimes the bottoms of the uprights are not at all mortised into the sole-tree, but rest flatly upon them, being kept in their places by pressure and friction only.

At a few places the chamber-frames are made of *angle-iron* riveted together. This plan has the advantage of presenting an extremely durable and clean erection, and the injurious action of any wooden parts keeping the lead from cooling cannot exist here. But this kind of plant is costly to erect and to keep in order by frequent painting; the fastening of the straps is also more difficult than with wooden frames. It has therefore made very little way, much less than iron frames for Glover and Gay-Lussac towers (*vide infra*).

Whether cross rails are used or not, in any case there should be diagonal stays, to give more stability to the frame. It is not of much consequence how the stays are put, so long as this is done according to the well-known rules of carpentry.

If, as is usual in England, the chambers are in the open air, one side of the frame is made about a foot higher than the other, so that the rain-water and melted snow can run off, and on the lower side a water-spout is arranged in such a way that the rain-water cannot run along the chamber-side down into the acid at the bottom.

Now the *chamber* itself can be erected. For this, sheet lead as wide as the rolling-mills can supply it, and of convenient length, is used, so as to have as few seams as possible. The usual strength in England is 6 lb. to the superficial foot, sometimes

7 lb., especially for the ends and the top, or for the first chamber of a set.

This thickness is sufficient for a chamber to last upwards of ten years; the bottom lasts longest, because it does not get so hot as the sides and the top, and because it is more protected by the mud of lead sulphate which collects upon it; only in cases of gross neglect (for instance, if nitric acid gets to it) it is quickly worn out, whether the lead be thick or thin.

In America the usual thickness of lead is only 5 lb., and even 4 lb. lead is sometimes used (Journ. Soc. Chem. Ind. 1885, p. 27); but this seems very bad economy indeed, and it can only be done when burning brimstone. In the best American works I have found 6 lb. lead.

On the other hand, at some of the best English works not only is 7 lb. lead used throughout for the chambers, but in the most exposed places, such as the front and back ends of the leading chamber and several feet of the sides adjoining these, 9 lb. is used. Sometimes the side sheets are rolled so that the upper and lower two feet are made stronger than the remainder, because these parts are more quickly worn out. Chambers built in this careful way last upwards of 20 years.

The *quality* of the lead is certainly not indifferent. As we have seen in Chapter III. (p. 44; comp. also Appendix), opinions are not altogether agreed as to the point whether pure or impure lead better resists the action of sulphuric acid; and in the present case it is no doubt not so much this acid as the nitrous compounds to which the attack of the lead is due. On the whole most manufacturers incline to the belief that "hard" lead is better adapted to vitriol-chambers than "soft lead." A test sometimes performed consists in trying which of several samples of lead in contact with sulphuric acid gives off more hydrogen from a given surface in a given time; but this test is very apt to mislead, and there is really no good test known as yet (Comp. Journ. Soc. Chem. Ind. 1884, p. 230, and the Appendix to this volume).

All sheet lead before being used should be "mangled" in order to beat out all inequalities and indentations casually produced in transit &c. For this purpose it is tightly rolled round a wooden roller, about 6 inches thick, and is beaten all the time with a plumber's mallet.

The sheets of lead were at first joined together by the ordinary

soft solder, which is very convenient for use, but is soon corroded by the acid. Places soldered thus are also much more brittle than pure lead. So long as the chambers had to be put together in this way, there was occasion for innumerable repairs.

Another plan (which is much better in this respect, but takes much lead, and is only easily applicable for straight seams) is the *rabbit-joint*. The edges of two sheets of lead are turned over in the way shown in fig. 109, put into one another, and beaten

Fig. 109.



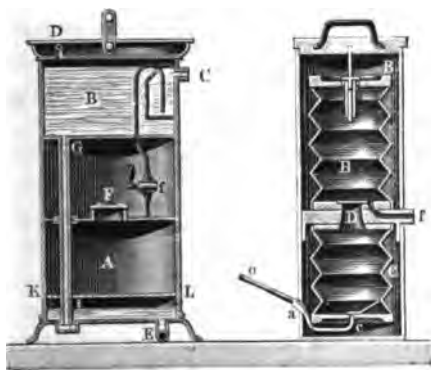
down on a smooth surface. Such joints are gas-tight, and have been used here and there in England till within the last few years.

The kind of joint now generally used is that made by *burning*, with the lead itself—that is, by melting it with a hydrogen flame fed by compressed air. In this way the two sheets are joined so tightly, that with good work the joint, being thicker than the sheets, is actually stronger than they. If the work is rough and uneven, foreign substances will easily be deposited in the rough parts, by which the lead may be damaged.

This mode of joining was invented by Debassyns de Richemont. Two apparatus are required for this, whose construction is shown

Fig. 110.

Fig. 111.

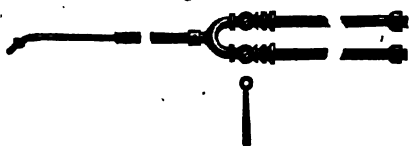


in figs. 110 and 111. Fig. 110 shows the "plumbers' machine"—that is, the hydrogen apparatus—quite similar to an ordinary

laboratory gas-holder, but made of lead, often with a wood casing. The lower vessel, A, contains a lead grating, KL, upon which granulated or scrap zinc is put. The upper vessel contains dilute sulphuric acid. The connecting-tube with a cock *f* allows the gas to pass out of the opening C, after it has first got washed in a water-vessel. Often there is a plain outlet just above the cock *f*. The outlet is connected with a long india-rubber tube, by means of which the gas can be conducted to a distance. The tube G serves for running sulphuric acid from B to A. It can only run in as gas is allowed to escape by opening the cock *f*; and thus a continuous current of gas is obtained. The openings D, E, and F serve for introducing acid and zinc, and for running off the solution of zinc sulphate.

The second part of the apparatus, which is shown in fig. 114, is simply a portable smith's-bellows of cylindrical-shape, the lever of which, *o a c*, a boy works with his foot. The air is forced through the valve D from C to the closed air-vessel B, and escapes through the opening *f*, likewise connected with a long elastic tube. The two tubes are united by the blow-pipe, fig. 112; and the mixture

Fig. 112.



is ignited. Each limb of the blow-pipe is provided with a stop-cock, by turning which the plumber may admit more air or hydrogen at will, and thus can produce a flame of any size, which, however, should never be an oxidizing one.

The mouth-piece of the blow-pipe itself is sometimes connected with the fork-shaped piece by a short elastic tube, to make it more mobile. Besides the ordinary mouth-piece, ending in an aperture of about $\frac{1}{25}$ of an inch diameter, the plumber also carries another, provided with a small brass shield, to obtain a steady flame in windy weather. The gases unite only immediately before escaping; and thus the flame cannot strike back. By means of this machine a pointed and very hot hydrogen flame is produced, which, at the place where it touches, melts the lead immediately down to a certain depth; and the art of burning consists in touching and

melting parts of two sheets *at the same time*, which, on cooling, solidify to a whole.

It has happened that plumbers have been poisoned by arseniuretted hydrogen, produced by impurities in either the zinc or the sulphuric acid. The hydrogen can be freed from this by washing it in a solution of cupric sulphate, by which the arsenic is precipitated.

The *burning* itself is a kind of work requiring much practice, because the plumber must not allow the flame to act a moment too short a time or too long. If he does the former, the fusion is not perfect and the seam is not tight; if he does the latter, he burns a hole in the lead. Wherever it is possible, one sheet is laid about 2 inches over the edge of the other, as shown in fig. 113. The

Fig. 113.



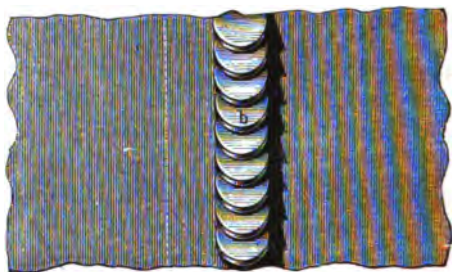
seam is made with the help of a strip of lead, about $\frac{5}{8}$ by $\frac{1}{4}$ inch thick, which the plumber holds in one hand whilst he guides the blow-pipe with the other. He works in this way:—He touches with the flame the place *a* (fig. 113), where the edge of one sheet lies upon the other, so that the surface of the lead (previously scraped clean) just melts, but the back part of the lead does not melt. At the same time he holds the above-mentioned strip in the flame, so that drops fall from it on to the just-melted part of the sheets, and the whole is united into a seam, *b*, all fusing together into one mass. By a slight motion of the wrist the plumber removes the flame for a moment, and the lead, which has only just been melted, at once solidifies; in another second the flame is again directed upon the lead, and a new drop flows partly over the first one; so that at last the whole seam takes the shape shown in fig. 114.

Although all this is much more easily described than carried out successfully, still the burning of *horizontal* seams is learned in a comparatively short time, and can be done very quickly by a practised workman. In windy weather it is certainly much more difficult, and in rainy weather it is not possible at all.

The burning of *perpendicular* (upright) joints is much more difficult, and, even in the hands of the most experienced workman,

takes at least three times as much time for the same length of seam as horizontal burning, without ever being as strong as the latter. This is easily understood ; for the melted lead, which quietly remains lying on a horizontal sheet, in upright burning at once runs down ;

Fig. 114.



and this can only be prevented in one way : the lead must be heated exactly up to the melting-point, and the flame instantly removed till the seam has solidified ; and the burning must always be done from the bottom upwards, so that to a certain extent the seam will retain the drops of lead. In this case much use cannot be made of strips of lead for strengthening the seam.

A practised plumber can burn as much as 10 feet upright or 25 feet horizontal joints in an hour ; but such figures are only reached in piece-work.

The way of building a lead chamber in England is usually as follows :—The commencement is made with the sides, for which the sheets are made as wide as possible (most lead-rolling mills supply them up to 7 feet 9 inches, some even wider), and so long that they extend 4 inches beyond the height of the chamber, of course taking into account that one side of the chamber is a foot higher than the other. 6 inches are reckoned to turn over the crown-tree ; but 2 inches are saved at the bottom, because the lead afterwards expands by the heat of the chamber.

Now, on the wooden floor before mentioned a wooden table (the “sheet-board”) is constructed, held together at the back by battens, but completely smooth on the upper surface. It has the width of two or three sheets of lead (that is, 15 feet 6 inches, or 23 feet 3 inches) and the height of the chamber—which, of course, can only be done when (as is generally the case) the chamber is at least

as wide as it is high. On this table the sheets of lead are rolled out flat, placed side by side, so that one overlaps the other 2 inches, and burned together; at the same time all the straps (of which we shall speak directly) are burnt to the lead, which can be done because the upper surface will afterwards be the outer one. The upper edge is bent round the sheet-board, so as to hold it fast; and when everything is finished this end is wound up by a set of pulleys, so that the sheet-board is raised along with the sheets of lead, and lies flat against one side of the chamber-frame. Now the upper edge of the lead is at once bent over the crown-tree and nailed down, as well as all the straps. For this no cut or wire nails are ever used, but wrought nails with broad heads ("plate-nails"), about $1\frac{1}{2}$ inch long, whose heads are all protected against the acid by dipping a few at a time into melted lead. When the lead has been completely fastened to the frame, the sheet-board is lowered down, moved forward its own width, and another piece of the chamber-side made upon it, till in this way the chamber-sides and ends have been finished all round. Only in the corners it is preferable to use single sheets, which form a rounded corner: this is much stronger than a sharp edge. The object of the described process is this, to reduce the upright burning to a minimum. It is much better than the former plan of hoisting up each single sheet, turning its margin over the crown-tree, and unrolling the sheet by its own weight. In this case every single sheet had to be joined to its neighbour by upright burning, and the straps had to be burnt on in an equally inconvenient manner. If at all possible, the seams ought not to be behind the uprights, so as to be better accessible for repairs; and for this reason also it is to be recommended to make the chamber-frame as shown in fig. 106, 107, or 115, where the uprights do not touch the lead at all.

The *straps of the sides* must be arranged according to the style of the frame. If this only consists of uprights mortised into the crown- and sole-trees, without any cross rails, the straps consist of perpendicular pieces of lead, nailed sideways to the uprights with five leaded nails each. The strap ought to be long enough to turn over the edge of the upright, so that two of the nails come to the front (fig. 117, upper part). Such straps are placed alternately on one and on the other side of the upright, one about every 4 feet. These straps do not allow the chamber-lead to follow the changes

Fig. 115.



Fig. 116.

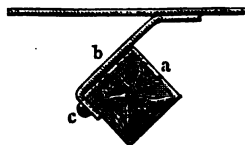
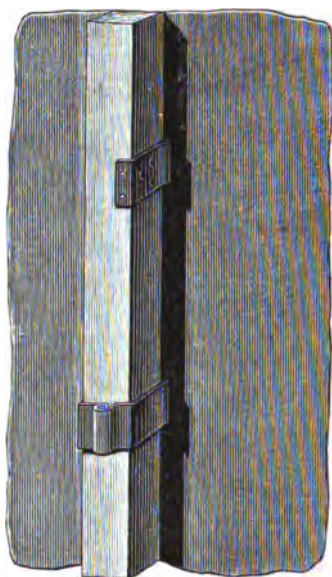


Fig. 117.



of temperature by extension or contraction. This easily leads to deformation of the sides and tearing off of the straps; and it is therefore better to avoid this style, which can be done by only nailing down the top strap in this way. For the lower straps longer pieces of lead are burnt to each side of the upright, which meet on its front, and are there joined by rabbeting (see fig. 117, lower part, and fig. 118). There are no nails used here; so that the lead walls may move up and down the upright, whilst at the same time they are all the more stiffened by being held fast in two places. This, of course, takes more lead and labour than simple straps. In each case the straps are about 8 inches in depth.

The object of keeping the lead clear of the wood, and of giving it scope for expanding, is well attained in the form of strap shown in figs. 115 and 116. The upright *a* is placed with one of its edges pointing towards the chamber. The strap *b* turns round the edge of *a*, and is fastened to it, not by ordinary nails, but by a broad-headed pin *c*, which passes through a slit of 2 inches height. This arrangement allows the strap to work up and down, as the chamber-side expands and contracts.

If the frame is provided with horizontal cross rails, there are only a few upright straps used—sometimes none, only horizontal ones, turned down over the rail, and nailed to it (fig. 119) two of 6 inches length for each rail. This style of straps protects the chamber-sides much better against deformation than the upright straps, and carries the weight better upon the frame; it also permits the lead to be kept further apart from the wood, since the straps may leave about $\frac{1}{2}$ inch (not more) space between the lead and the rails. The diagram shows this.

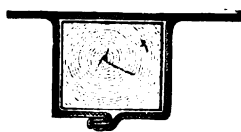


Fig. 118.

The chamber-sides can also (as at the Thann Works) be made of horizontally disposed sheets of lead. The overlap in this case is nailed to the horizontal cross rails in lieu of straps, as shown in fig. 120; but first the whole height of the chamber-side is finished, the whole is rolled upon a wooden roller, and allowed to unwind itself by its own weight from the top. In this way there is not so much pull upon the seams as if the chamber were made of sheets hanging down by their length, since each sheet is supported just in the place where there would be a pull. This plan, indeed, seems

Fig. 119.

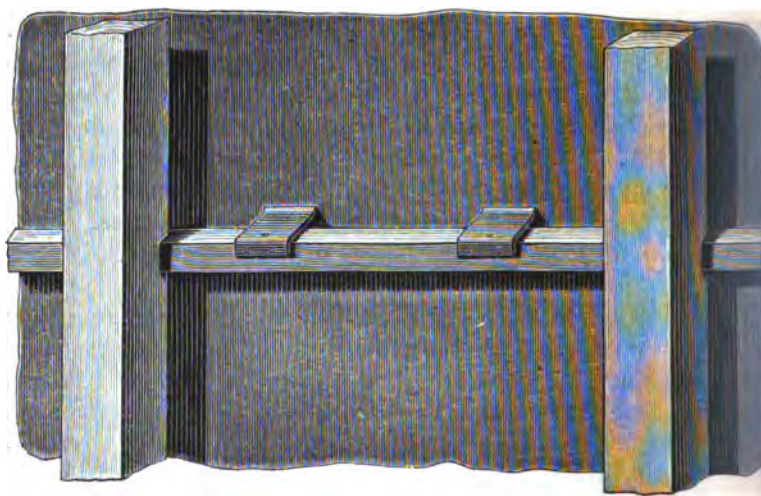


Fig. 120.

to be worthy of general recommendation; for it saves the lead and labour of all the straps, and supports the chamber very well.

At least as substantial is the plan used at Aussig. There are no side-straps at all; but to each upright of the frame corresponds a strip of lead burnt to the chamber-side along its whole height, probably the lap turned outside. This is nailed sideways to the upright. Between this and the lead there is a wooden lath, to increase the contact of air with the chamber-lead as much as possible. Fig. 121 shows this in horizontal section.

Fig. 121.

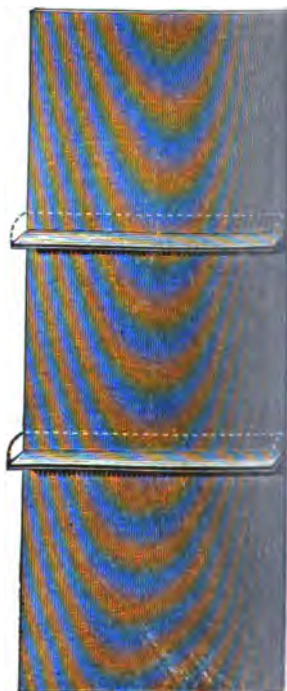
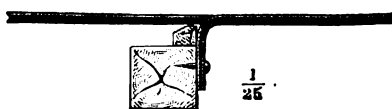




Fig. 123.



Fig. 122.



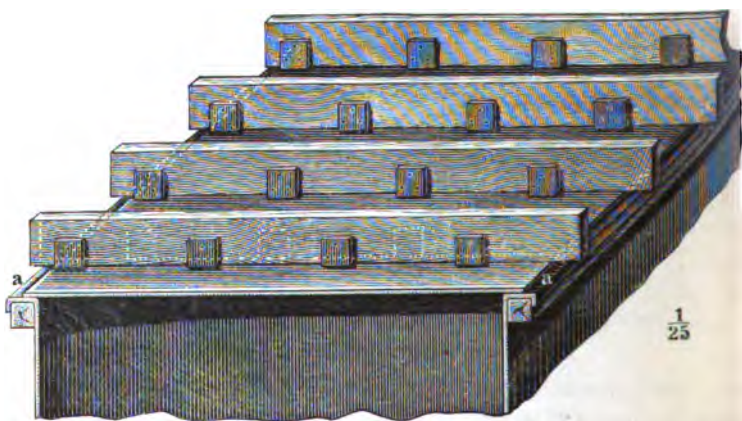
Fig. 124.

Mr. Benker ascribes great advantages to his *perforated straps*, shown in figs. 122 to 124. Fig. 122 is a plan, showing the chamber-side *a*, the uprights *b*, the cross-bars *c*, the small wooden bars *d*, and the straps *e*. The same parts are seen in vertical section in fig. 123. The chamber-lead is kept 2 or $2\frac{1}{2}$ inches apart from the cross-bars; the perforations of the straps (which may extend the whole width of the cross-bars, as in fig. 125) cause a

strong current of air to rise upwards and cool the lead, without allowing any quantity of dust to accumulate on the straps. This system is especially good for chambers which are driven hard for "forced work."

In the first-described case, now generally used in England, at first only about a yard of the seams is burned, and that at the top, so that the chamber can be covered in and the remainder can be done at leisure in bad weather. The next thing, therefore, is the *chamber-top*. For this we need a temporary scaffolding, movable on wooden rollers, made of high trestles joined together at the top, equal in height and width to the chamber, and in length to at least two (or, better, three) sheets of lead. This scaffold is put together within the chamber itself, its separate parts being got in by bending back one of the side sheets. It is covered on the top with a flooring of boards; and upon this the sheets serving for the chamber-top are flattened out. These are a little wider than the chamber, so that they project 3 inches on each side. Thus they do not project quite as far as the overlap of the side-sheets (6 inches), and there remains a joint suitable for burning (fig. 125, *a*), which is burned very strongly. Now the sheets

Fig. 125.



themselves are joined by burning, and all the top-straps are burnt out. The latter serve for fixing the chamber-top from above to the top joists carrying it. The latter, for a chamber 20 to 26 feet wide, are 3 to 4½ inches thick and 10 to 12 inches high, and are placed at distances of 14 to 18 inches from centre to centre. Their

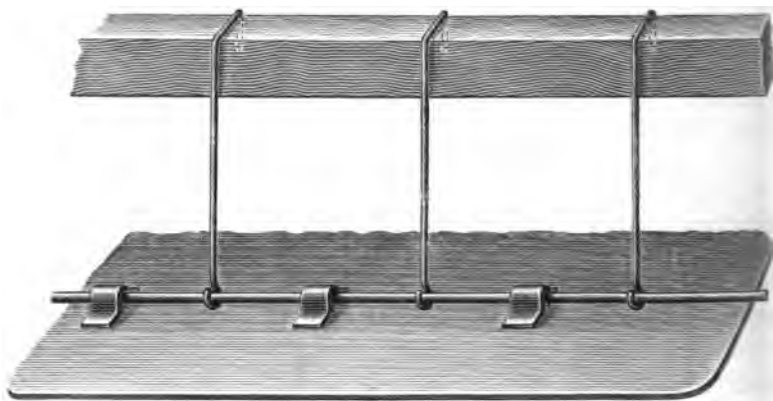
length is at least sufficient to reach to the outside of the crown-trees; it is better if they even project a little beyond, to have a good support. The straps themselves are made 7 inches square, and stand alternately on both sides of the top joists, about 3 feet apart on each side. At other works there are fewer but longer straps. They are bent up and nailed to the top joists laid above them on edge, with five leaded nails each. When all this has been done, the top joists, by the help of the straps, carry the lead of the chamber-top, and the joists themselves rest upon the side frames, but separated from them by the overlap of the chamber-sides. It is preferable if the joists are well clear of the chamber-top, so that air can circulate between lead and wood.

The top joists are protected from canting over by a few boards nailed across them, which at the same time serve as a passage on the chamber-top. Where the chambers are roofed in, mostly longitudinal sleepers are laid on the top, joined to the top joists by iron clamps, and the whole suspended from the timber of the roof, which must be made strong enough for this purpose; but some hold that even with roofed-in chambers it is safer to keep the chamber-top independent of any movement of the roof.

Where the chamber is too wide for any single cross joists, two lengths of these must be joined together and trussed, according to the rules of carpentry; in this case trussed girders may run across the width of the chamber, and the proper joists, to which the top lead is fastened by straps, run parallel with the long sides of the chambers; they are either morticed into the girders, or (which is the stronger plan) they rest in cast-iron shoes bolted to the girders. This, however, is only required for chambers standing in the open air; it is not very convenient, as the side frames have to be weighted very much. Such wide chambers, as we shall see below, have not altogether turned out well.

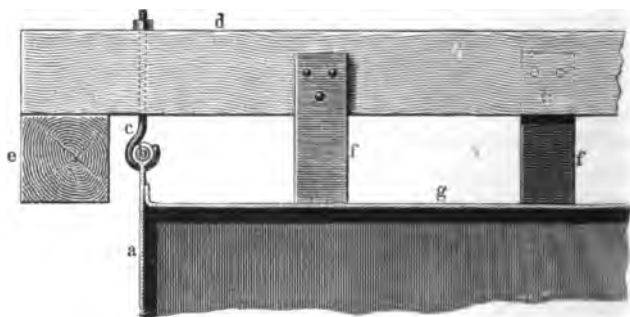
Quite different from the just-described chamber-tops are those found in many continental works. There are no wooden top joists, but, in the place of these, thin iron rods about $\frac{1}{2}$ in. thick, fastened to the chamber-top by a lead covering burnt on each side to the chamber-lead. These horizontal rods themselves are suspended from the roofing by means of $\frac{1}{4}$ -inch rods placed at short distances from each other. This system cannot be employed for chambers standing in the open air, as it makes the chamber-top dependent upon the beams of the roof; it is shown in fig. 126.

Fig. 126.



Another system, which may, or may not, be connected with the roofing, is the following (fig. 127) :—The chamber-side *a* is carried somewhat higher up, and bends round an iron rod, *b*, $\frac{7}{8}$ -inch thick, the part coming back over the iron being burnt to the other lead. Here and there holes are left for the passage of the iron hooks, *c*, which are bolted to strong joists, *d*. The latter may form part of the roof, or they may be supported quite independently on the crown-tree *e*. The straps *ff* hold up the chamber-top *g*, and prevent it

Fig. 127.



from sagging ; the clear space between *g* and *d* is about 8 inches. The object of this arrangement is to prevent all contact between lead and wood even at the top edges of the chambers.

At the Griesheim works, in Germany, the following very rational

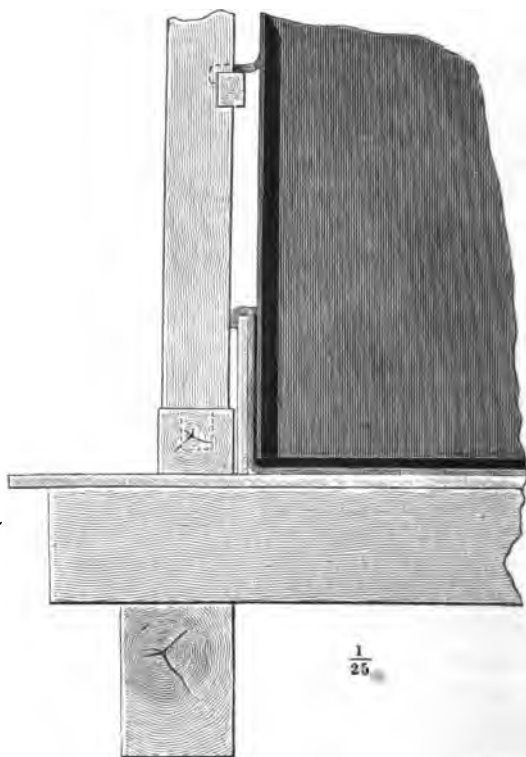
plan of erecting lead chambers is followed. On a staging of the whole area of the chamber-bottom, but raised over its top, first the chamber-ends are made; over these, without removing the ends, the chamber-sides are made, first one, then the other, and last of all the sheets composing the top are laid down and burnt together. Thus ultimately five layers of lead are lying on the staging one above another. Then the top straps are burnt on and are joined to the top joists, which are put in their respective places. The whole lead-work is now hung from six differential pulleys and the staging is removed. As this is done, the ends and sides drop down into their places, and need only be joined in the corners, where they are bent in at an obtuse angle. This mode of procedure causes nearly all the burning to be horizontal, so that the work is done more quickly, cheaply, and substantially.

The *chamber-bottom* is left to the last; and it happens no doubt very rarely (in England probably never) that, according to older prescriptions, the bottom is laid down first and protected by straw and boards while the remainder of the chamber is being made. It is, on the contrary, made last of all, but not always in the same way. In some works the side sheets are burned to it all round, and openings are left in a few places for drawing off the acid, for taking samples, &c. In the majority of works the bottom is independent of the sides, and forms an enormous tank with turned-up sides, into which the chamber-sides hang down, dipping into the bottom-acid, and thus forming a hydraulic joint. This allows the chamber-sides to expand and contract with the temperature, and also makes the bottom-acid accessible from all sides, so that it is generally preferred in spite of the larger expenditure of lead; but recently a good many works have adopted the first-mentioned plan of making the chamber as a closed box, which saves both lead and the trouble unavoidably connected with the second system. Often the upstand, or "lag," which ought not to be less than 14 inches high, so as to afford a good deal of room for acid, is made from a narrow sheet of lead of double width, by bending up one half and leaving the other half to form a portion of the chamber-bottom; the latter is then finished by burning it together with other sheets of lead. This is more convenient for the plumber than taking sheets equal in length to the width of the chamber, along with the height of the upstand on each side. The latter must not be left loose, because it is easily bagged out by the side pressure of

the acid ; but a 1-inch board is placed all round the chamber-floor, over the edge of which the upstand is turned round and nailed down. This is shown in fig. 128. Instead of a solid board, it is preferable to employ merely a number of perpendicular or horizontal rails, which admit the cooling-action of the air upon the lead.

In some works the bottom is divided into two, three, or four parts by partitions of the whole height of the upstand. The object of this is, not to empty the whole chamber in the case of repairs ; but it is very rarely done, as this arrangement prevents a free circulation of the acid, and as the bottom mostly suffers less than any other part of the chamber—excepting through gross neglect,

Fig. 128



by the formation of nitric acid, which ought not to happen at all.

In England, where the winters are not severe, lead chambers are

hardly ever roofed in, but are only built so that the rain-water can run off as described above. But even then the space between each two chambers must be covered by a light roof, and the whole set must be surrounded by a wooden shed, because a gale might tear the lead off the frames, or even throw down a chamber altogether. These wooden houses have windows or Venetian blinds, changed according to the wind. In windy places they are always made first, as soon as the foundations and the frame are finished, but before the lead has been fastened to the latter, because during the building the incomplete chamber is even more exposed to being thrown down by a gale than after completion.

Thus the chamber-tops are exposed in England to the heat of the sun in summer and to the snow in winter; this is possible because neither of them occurs to an excessive degree. In the less windy places even the chamber-sides are sometimes left without protection against the weather, but never so in well-arranged works. In the south of France, on the other hand, the chamber-tops are always protected against the sun and the rain by a roof; but the sides are always exposed, which, on account of the heat of the sun there, is certainly very wrong. In the north of France, in Belgium, and in Germany the chambers are always completely enclosed in buildings, usually of a very light construction.

Renewal of the Chambers.—The greatest wear and tear is experienced in the first chamber, more especially at the front end, and, as some assert, even more so at the back end and the immediately adjoining part of the sides. Hence the first (leading) chamber is often made of stronger lead than the others. Besides, it must be noticed that any angular parts of a chamber wear out more quickly than round or straight portions. The upright corners are therefore always broken or rounded off; but this is not easily possible with the horizontal top corner. Hence, at some works they make the lead stronger in that place (p. 344). The plan of making the roof partly slanting (*vide infra*) may do some good in this respect as well, as this avoids a sharp corner. The part dipping in the acid, and alternately subjected to this and to the action of the air, is also liable to quicker wear. There is general agreement on the point that any part of a chamber which gets hotter than the remainder will wear out much more quickly; and this should be guarded against in the construction of the chamber-frame (*suprà*, pp. 342, 351, 356).

Special observations on the wear and tear of lead chambers have been made by Burgemeister (Chem. Zeit. 1889, p. 1633). A set of two chambers was observed after $23\frac{1}{4}$ years, during which time the larger chamber had been at work with brimstone for 32 months, with pyrites (first Westphalian, then Rio Tinto) for 178 months, idle for 75 months. The thickness of the lead was originally 2.57 mm., at the end of the period on an average only 1.88, that is a loss of 0.69 mm. or 26.8 per cent. The part dipping into the bottom-acid was most worn; next to it the places where the lead was double or where it was protected against cooling by the wooden frame. For this reason it is best to burn the joints outside, because in this case the inner part of the lap-joint is eaten away first without injuring the joint; if the joint is burned inside, the lap is loose on the outside, and as soon as the inner part is eaten away the chamber must leak. The bottom of the chamber, which is protected by the acid, suffers least. A small chamber which was placed between the Glover tower and the large chamber, and which was kept at a higher temperature (from 65° to 90° C.), had lost in 120 working months as much as 17.65 per cent. of the thickness of lead.

We have constantly laid stress on the point that the lead should be clear of the woodwork on all points, both because it is thus longer preserved by the cooling-action of the air, and because it is accessible to the plumber. But this condition can, of course, be realized only for the sides and top, not for the bottom. Fortunately the latter suffers least, being protected by the acid itself and by a layer of sulphate of lead. If, however, a leak occurs here after all, it is very awkward to repair. Sometimes this can be done by measuring its distance from the sides, cutting a hole in the chamber-top and dropping down a bucket-full of plaster of Paris or, preferably, of a mixture of fresh and burnt pyrites-dust, which quickly hardens into a cake and may stop the leak for years to come. But if this does not succeed, there is nothing left but stopping and emptying the chamber, and entering through the man-hole in order to get at the bottom.

A chamber will last very much longer if the frame be made substantial, and the straps be well burnt on and nailed down and numerous enough, so that they will not be readily torn off. Should this happen, the mischief must be repaired at once: nowhere does the saying come more true "that a stitch in time saves nine."

If the repair is put off too long, the chamber-lead, pulled by its own weight, wrinkles irregularly, and the chamber becomes unfit for work much too soon. Especially those parts of the frame most exposed to the action of the acid must be carefully looked after, and, in case of need, at once repaired, before the parts of the lead sides dependent upon them have lost their support and have collapsed. This is most necessary at the junctions of connecting-pipes, at the places where the acid is siphoned off, &c. The wind must also be kept off, and any loose pieces in the bratticing round and between the chambers promptly put right; a gale of wind may tear off the straps of a whole chamber-side at once or force the frame to one side. The gangway round the chambers ought to be wide enough (say 5 feet) to admit of easy control and repair.

It used to be reckoned that with 6 lb. lead in normal circumstances a chamber will generally last from eight to ten years, but with many repairs during the latter years. But since the art of building, and more particularly of *managing*, vitriol-chambers has become better understood, they have been made to continue much longer in use. On the Continent, where they are not (or formerly were not) so much strained as is frequently the case in England, vitriol-chambers generally last much longer than the above term, viz., 20 or even 30 years; but even in England this is found to be the case at some works where the chambers are built with more regard to durability than to economy in first cost.

There is no doubt whatever that, all other things being equal, a chamber lasts longer in proportion as it is less heated; it is not so much the heat itself, but the intensity of the chemical reactions going on within the chambers which produces the heat, and moreover the increase of the action of all chemicals by the elevation of temperature brings about the same result. It is only another way of stating this fact, if we say that a chamber lasts all the less time the more nitre is sent into it and the more acid is made in it.

In the case of chambers without a roof the top generally wears out first, then the parts dipping into the bottom-acid and the ends; the bottom remains good up to the last, unless nitric acid gets to it, which most easily happens in the last chamber, if its strength is allowed to run down too much.

When a chamber requires so much repairing and patching that it does not seem likely to pay, and when, after all, the escape of

the gas from the too numerous chinks and rents can no longer be kept down, it is very bad economy not to pull it down at once; for the yield of acid must fall off very much. In this case a temporary connexion is made between the two apparatus on either side of it, the acid contained in the chamber is worked down as long as it will run, a hole is cut into its side, and men provided with india-rubber boots are sent in to shovel up the *mud* lying at the bottom into a heap, from which a good deal of acid is still obtained by draining. The mud must now be removed; if the space underneath is free, a receptacle is formed by low banks of clay, a hole is cut in the chamber-bottom, and the mud pushed down. If this is not possible, it must be removed in a much more troublesome manner, by thickening it with sawdust and washing with water. In either case it is dried in a reverberatory furnace, sometimes with the addition of a little lime in order to prevent the escape of acid vapours. For all that, this operation usually causes a very disagreeable stench, probably owing to arsenic, selenium, &c. The dried mud, principally consisting of lead sulphate, is either smelted for lead in a small cupola heated by coke, or simply sold to the lead-workers.

After taking out the lead-mud, the chamber-lead is detached from the frame, and the good whole pieces rolled up for use as sheet lead; the others are melted in an iron boiler, the dross is skimmed off, and the lead cast in the usual pig-moulds; at the lead-rolling mills this lead is very well liked for other chemical purposes (see p. 145). Counting up the pig-lead, the dross, and the lead sulphate, usually nine tenths or upwards of the original weight of the chamber is recovered; the remainder has gone away in one shape or another with the vitriol made.

If the frame has been substantially made, it stands a second, sometimes a third lead chamber, with a few repairs, putting in odd beams &c. Of course, in case of any doubt, it would be extremely bad economy to run the risk of having to stop a chamber because its frame would not hold out as long as the lead.

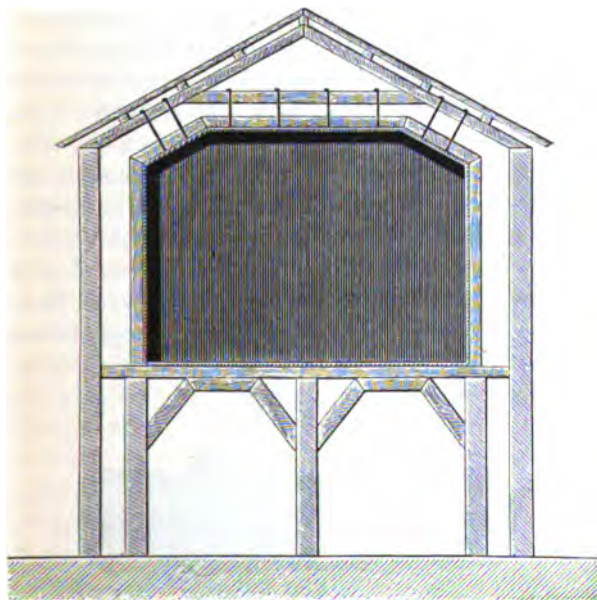
The *size of the chambers* varies very much. Apart from the "tambours" of the French system, the proper chambers are made with as little as 10,000 and as much as 140,000 cubic feet capacity. Such small chambers are no longer built as main chambers; the usual capacity of these may now be taken as ranging from 25,000 to 70,000 cubic feet, more frequently nearer

the upper than the lower limit. Smaller chambers cost much more, comparatively, than large ones, and do not afford any corresponding advantages.

The *shape* of the chambers is nearly always that of a long box of square or approximately square transverse section. At some places, in order to save lead, the chambers have been made up to 60 feet wide; but this is not to be recommended on any account. It causes difficulties in constructing the wood frame, and, what is more serious, the yield of acid in such large chambers is not so good as in those of ordinary shape, say between 20 and 30 feet wide. This is easily understood, as in such very large sections the gases do not get properly mixed, and there are too few surfaces offered for contact and cooling (see below).

For the purpose of saving lead, the chambers belonging to the different works of the Rhenania Chemical Company are constructed in the way illustrated in fig. 129—that is, with the top corners cut

Fig. 129.



off, to suit the slope of the roof. This admits of putting the largest possible height of chamber into a roofed building; and

Mr. Hasenclever also contends that the "dead corners" of square-sectioned chambers are thereby avoided. There is also less wear and tear than in the sharp corners of chambers of the ordinary square section (*comp. suprâ*).

The usual width of vitriol-chambers is rarely below 20 or above 30 feet; their height varies from 16 to 25 feet, or exceptionally a few feet more. Their length (always speaking of the principal chambers, not of the small chambers or "tambours" arranged before and behind these in the French system) is rarely below 100 feet, but may attain 200 or even 300 feet.

H. A. Smith, in a pamphlet on the Chemistry of Sulphuric-acid Manufacture (1873), endeavoured to prove that the upper space of the vitriol-chambers did no work at all, and that chambers of 3, 6, or at most 8 feet in height would be most suitable. His experiments (described and refuted in detail in our first edition, p. 285 *et seq.*) were decidedly inconclusive, and a practical test of his theory at the Oker works led to its entire rejection.

Sometimes the whole working space is contained in *one* chamber. Scheurer-Kestner (Wurtz, Dict. iii. p. 147) mentions a single chamber of 142,000 cubic feet capacity, and quotes the experience of several works, according to which it is quite unnecessary to divide the set into several chambers. Much more usually, however, several chambers are combined to form a set, which affords this advantage—that for repairs it is not necessary to stop the whole set. The single chambers are connected by round pipes or angular flues (tunnels). The former are preferable, because they can be made without a frame, and because they stand better. They must, however, be made of strong lead, say 9 to 12 lb. per square foot, and bound here and there with iron hoops, between which

Fig. 130.



and the lead wooden staves are placed in order to keep the pipes in shape; but if the weight of the lead amounts to 15 lb.

per square foot, no staves are needed. Fig. 130 will make this clearer.

The iron hoops serve also for suspending the pipes from beams &c. The *width* of the pipe introducing the gas into the first chamber, whether it comes from the Glover tower or from the burners, must be adapted to the quantity of gas conveyed. For a combustion of 7 tons pyrites daily a pipe of 2 feet diameter, for 9 tons one of $2\frac{1}{2}$ feet, upwards of that one of 3 feet diameter will do; more than 10 tons are rarely consumed for a single set in twenty-four hours. Since the volume of the gas decreases in its onward journey, the connecting-pipes between the single chambers may be successively a little smaller; but it is not well to grudge any thing here, since no harm is done if the pipes are too large, but very much if they are too small.

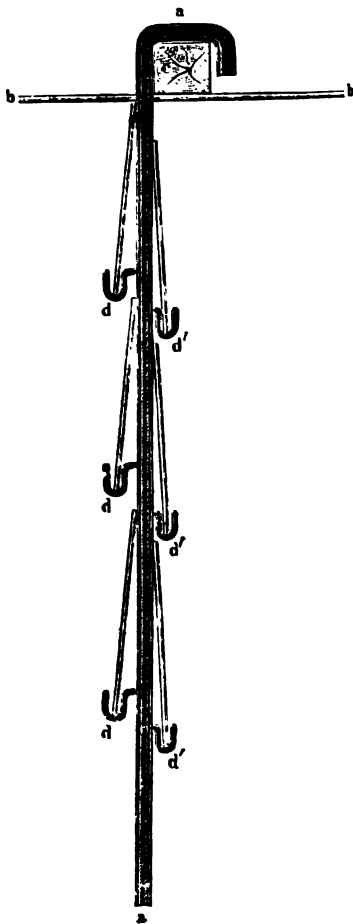
A great diversity of opinions exists upon the point how the single chambers are to be *combined to form sets*. Among the hundreds of vitriol-works very few will be exactly alike in this respect; and frequently even in the same works different combinations are found. We may, however, consider it as established that it is almost indifferent in which way the chambers are combined, if they are, in the first instance, properly built (that is, not too high or wide), and if, secondly, they possess a certain cubical capacity for the quantity of sulphur or pyrites to be consumed. Within these limits those combinations are best which require least lead, and which are laid out so as to afford the greatest facility for supervision. Of course there is also an ultimate limit to the capacity of the whole set; but opinions differ upon this point also. At some works a set consists of nine or eleven chambers of 35,000 cubic feet each; at others, equally large, it is limited to three chambers of 42,500 cubic feet each, &c. Thus at Hebburn-on-Tyne there are several sets of three chambers each, each of them 20 feet wide, 125 feet long, 17 feet high on one side, 18 feet on the other side; each set serves for 18 burners, burning 7 cwt. daily. At Gateshead there are several sets of three large chambers, each so arranged that two of them communicate separately with a set of kilns ("working-chambers"), and both of them are connected with the third chamber; the whole set has a capacity of about 200,000 cubic feet. More usually the gas passes through all three chambers in succession. Very often four chambers are combined, each of them about $20 \times 20 \times 130$ feet,—or five chambers, two of

them working-chambers, thus, $\begin{smallmatrix} 1-3 \\ 2-4 \end{smallmatrix} \rangle 5$,—or even six chambers, thus, $\begin{smallmatrix} 1-3 \\ 2-4 \end{smallmatrix} \rangle 5-6$.

On the whole it is not advisable to combine too many chambers and to make the sets too large, certainly not above 200,000 cubic feet; otherwise all the connections &c. must be too large, the first chamber becomes too hot, and any disturbances of the process are felt over too large an area. On the other hand, a set of less than, say, 130,000 cubic feet takes as much labour and auxiliary apparatus as a larger one, and will thus be more expensive. In a larger set any disturbances in the nitre, steam, draught, &c. are found out before the gas has got to the outlet, and thus can be more easily put right.

At some places, *e. g.* at Uetikon, near Zurich, there existed for a time a peculiar kind of chambers. Each set only consisted of one large chamber, 330 feet long; within this, however, there were two partitions, dividing it really into three chambers. The partitions are made as shown in fig. 131. A row of perpendicular

Fig. 131.



iron gas-tubes of 1-inch bore, covered with lead, *a*, is placed across the chamber, carried through its top, *b*, and hung from one of the joists *c*. At vertical distances of 2 feet there are lead hooks, *d d*, attached to the tubes, on the other side other hooks, *d' d'*, a little lower. These hooks must not be made of sheet lead, because they bend too easily, but they must be cast. On these hooks sheets of

glass 2 feet \times 2 feet 6 in. are placed loosely, leaving chinks of about 1 inch width for the passage of the gases, in order to mix them better. These partitions do not seem to offer any guarantee of durability; and in fact, both at Uetikon and at other works, formerly possessing similar glass partitions, they have been removed again; sometimes they are said to have suddenly collapsed and cut through the chamber-bottom.

The simplest kind of internal partition, a lead one, is not practicable, because the lead, exposed to the heat and the gas on both sides, is very quickly worn away. This entirely disposes of the suggestion of Bornträger (Chem. Ind. 1885, p. 386) to make nearly horizontal (rather slanting) partitions in the chambers, in order to multiply contact-surfaces.

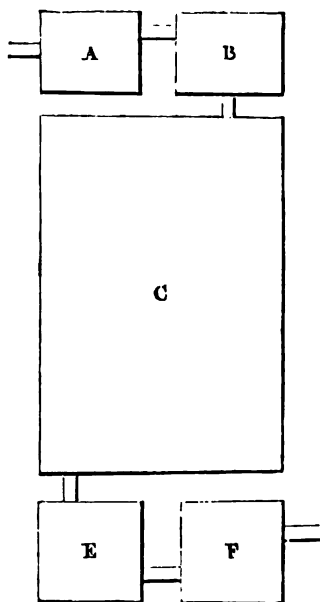
The different chambers of a set are either placed on the same level, or, more suitably, each following chamber is placed 1 or 2 or, better, 3 inches higher than the preceding one, so that the acid of the back chambers can be run more easily into the working-chamber. In this first chamber the acid is both strongest and most free from nitre; and it is therefore preferable to draw off any acid from this, whether it be for sale, for use, or for concentration. The acid drawn off is replaced partly by that newly formed in the same chamber, partly by the weaker acid run over from the other chamber. If there is only one long chamber, the acid is always found strongest near the entrance of the gas.

In England, mostly, all the chambers of a set are of equal size, apart from local circumstances; and this plan is now more frequently found on the Continent as well than formerly, when the French system, even now the more usual one, was the only one to be met with. In this system there is a "large chamber," C, fig. 132, placed at the lowest level, combined with a few small chambers at a higher level, both before and behind the large one. Thus the first small chamber or "*tambour*," A, serves for denitrating the nitrous vitriol by hot water; the second one, B, for introducing fresh nitric acid; the third and fourth *tambours*, E and F, for finishing the reaction.

In the south of France (Favre, 'Monit. Scient.' 1876, p. 272) there is mostly a large chamber of 135 \times 26 \times 20 feet, or of 100 \times 16 \times 22 feet, combined with two small chambers, together about 140,000 cubic feet. At Aussig each large chamber is 200 feet long and 24 feet wide, and is combined with a small

tambour for catching the fine dust, and two small end chambers, not receiving any steam, but only serving for cooling the gas previously to its entering the Gay-Lussac tower. The system con-

Fig. 132.



sidered the best at Oker (Bräuning, p. 136) is the following:—two tambours of 127 and 106 cub. metres, one main chamber of 1459 cub. metres, one back chamber (not fed with steam) of 162 cub. metres; total 1854 cub. metres. All the chambers are 17 feet wide and high; the main-chamber bottom is divided by partitions of 3 feet 3 inches height into 5 compartments. The connecting pipes are 18 inches wide; they introduce the gas at $\frac{2}{3}$ of the height, and take it away at $\frac{1}{3}$ of the height.

Some manufacturers reject all preliminary chambers, because the chamber process is carried on best if a large space is afforded at once for the mutual reaction of the gases. Thus in a large French works two thirds of the whole chamber-space are occupied by the first chamber, two ninths by the second, and one ninth by

the third; and this system has been followed at Uetikon as well for a number of years past with great success.

Small chambers, of course, require more lead and space than large ones of equal capacity. A preliminary chamber, however, is serviceable, where no Glover tower is present, for catching the dust and cooling the gas, so as to save the large chamber. For the same reason the nitric acid was formerly usually introduced into a special tambour; but it is best, as we shall see, to run it down the Glover tower.

A small chamber at the exit end is certainly serviceable for drying the gases previously to their entering the Gay-Lussac towers in cases where there is no long tube or tunnel for the above-named purpose.

The waste of lead in small chambers is more easily seen in a definite example. A chamber of $100 \times 20 \times 20$ feet has a cubical capacity of 40,000 cubic feet and a surface of 8800 square feet. A tambour of $16 \times 10 \times 10$ feet has a capacity of 1600 cubic feet and a surface of 840 square feet. Its contents are therefore $\frac{1}{25}$, but its surface almost $\frac{1}{10}$ of that of the large chamber; and consequently its surface is nearly $2\frac{1}{2}$ times as large, in comparison with its capacity, as that of the large chamber.

Whilst, of course, there is no doubt that a given cubic space of chamber-room is more cheaply obtained with a few large than with a greater number of small chambers, it is, on the other hand, very easy to overstep the mark in this direction. We have seen above that, in the case of chambers of an excessive section, the gases do not get properly mixed; but the same principle applies even to the division of the chamber-space in the direction of its length, since every time the gas has to be compressed into a comparatively narrow connection-tube in order to pass from one chamber to another, this must bring about a good mixture superior to that produced in the same length of undivided chamber-space. For this reason, to begin with, it seems expedient to subdivide the chamber-space by multiplying the number of chambers; and we shall further on meet with another strong reason for the same purpose, namely, that the cooling down of the contents of the chamber, essential for the reaction among them, is promoted by their contact with the comparatively cool end-walls of the chambers.

When speaking here and elsewhere of "*chamber-gases*," we

always comprise in them not merely the *vapours* of water, nitrous anhydride, &c., but also the *misty* particles of liquid sulphuric acid, nitrosulphuric acid, &c., floating about in the atmosphere of the chambers.

Schertel, in fact, starting from the basis adduced by my experimental and theoretical basis, to which he agrees, proposes to multiply the number of chambers, keeping them rather short (Chem. Ind. 1889, p. 80). Bode (Zeitsch. f. angew. Chemie, 1890, p. 11), on the same principle, proposes chambers of half the usual length, but twice the ordinary width—say 40 feet. This would involve some difficulties, although not insuperable, in constructing the chamber-frames. Later on (Sächs. Jahrb. 1890, p. 148) Schertel described practical experiments bearing out the theoretical considerations just mentioned; and further experiments on the manufacturing scale, entirely confirming my own results and conclusions, have been made by Retter (Zeitsch. f. angew. Chem. 1891, p. 4).

In the usual case, where a set of several chambers is combined to form the vitriol-making apparatus, the question arises how the single chambers of the set are to be connected. One thing about this is certain: that the connecting-tubes must be placed at the small ends, so that the gas shall travel right through the length of the chambers, and no dead corners are left. But the next question is, at what part of the section the connecting-tubes are to leave or enter the chambers. There is general consent as to this, that the gas should enter the first chamber near its top. Some proceed in this way: they take the gas away at the other end near the bottom and introduce it into the next chamber near its top. Others maintain just as strongly that this is wrong, and that, on the contrary, the gas-pipe ought to leave each chamber near its top and enter the next chamber near its bottom. Others, again, contend that it matters very little where the gas enters and leaves, and that it is therefore the simplest plan to make straight connecting-tubes about midway in the height of the chamber. This last view seems to be borne out by the practice of several practical men of very large experience, and it agrees very well with the investigations of Lunge and Naef (*vide infra*), who found that the composition of the chamber-gases in any given cross-section of the chambers does not differ very materially between top and bottom, so that it must be indifferent where the connecting-tubes are placed.

At Griesheim there are several connecting-tubes between the chambers instead of one. This seems very rational, and still at the same time serves for partially cooling the gases in their transit, which we shall find further on to be an important feature. "Dead corners" are most easily avoided by this plan.

The total *cubical contents* of a set of chambers must bear a certain proportion to the quantity of acid to be produced, several special circumstances modifying that proportion. Thus it is certain that for pyrites more chamber-space is needed than for sulphur; we have seen above (p. 313) that the relative proportion may be stated as 1 : 1·314. But now the question is, What is the absolute amount of space needed? Properly speaking, the connecting-pipes, if they are of great length, and the Glover and Gay-Lussac tower ought also to be included in the calculation, and that to a larger extent than corresponds to their cubical contents.

The consumption of nitre also influences the chamber-space; within certain limits a larger consumption of nitre may compensate for a smaller space.

Partly from this the widely divergent views on this point may be explained, but not entirely; for some manufacturers obtain about the same yield as their neighbours possessing half as much chamber-space again, although the pyrites, the general construction of the plant, and their consumption of nitre are as nearly as possible the same. In the following we shall reduce all statements to cubic feet of chamber-space required for burning 1 lb. of sulphur daily, taking, in the case of pyrites, the sulphur bought, not that actually burnt.

Schwarzenberg states the proportion for a small set of chambers and for *brimstone*, without a Gay-Lussac tower, to be 32 cubic feet for 1 lb. brimstone, with a consumption of 6 per cent. nitre; as the lower limit he states 29 cubic feet—even less in larger works, of which he gives some actual figures, viz. 22·8, 24·6, 24, down to even 16 cubic feet; but in the latter case much more nitre was used or acid was lost. Knapp (*Chem. Technologie*, i. part 2, p. 337) states 17·2 to 23 cubic feet. Fournet, at Bordeaux ('*Rapport du Jury international*,' 1867, vii. p. 18), states that in chambers of 400 cubic metres capacity he daily burned 500 kilograms of brimstone (= 12·8 cubic feet per lb.) with the assistance of several pipes filled with coke, and that his yield was 300 o. v. on 100 brimstone.

For *pyrites* Schwarzenberg states that the theoretical proportion for small chambers = 42 cubic feet, for large ones = 36·8, on each lb.

of sulphur actually burnt, or, say, 34·4 per lb. of sulphur bought. Bode states as the figure found in several German works 29·6 cubic feet per lb. of sulphur bought, with a consumption of 4·75 per cent. of nitre (which is now much smaller). From sundry English alkali-works I can state the following proportions (1879) :—

I.	II.	III.	IV.	V.
28	25	20	18	16 cubic feet.

I. and II. were considered too high by the chemists of the respective works themselves; but it should be stated that the same space was employed in 1864, when 30-per-cent. Irish pyrites was used, for which it was more suitable. III. (viz. 20 lb.) is a proportion employed at many large works; but IV. and V. are found in works having as good a yield of acid (270 to 288 o. v.) and no larger consumption of nitre ($3\frac{1}{2}$ to 4 per cent.). In all cases rich Spanish or Norwegian ore was burnt, and both Guy-Lussac and Glover towers were used. From this it follows that under the same conditions 20 cubic feet per lb. of sulphur charged is amply sufficient, and 18, or even 16, will do; but the latter certainly is generally assumed to be the lowest allowable limit. This agrees with a statement of Wright's (Chem. News, xvi. p. 94), who demands 16 to 19·2 cubic feet.

From the Inspectors' Alkali Reports it will be seen that the amount of chamber-space actually employed at English works varies in a most extraordinary way, and not merely in consequence of the fact that very small works generally employ an excessive chamber-space. It is also seen from the same source that the usual assumption that less chamber-space is used with brimstone than with pyrites is altogether erroneous. We will here give merely a few figures obtained by taking averages of the single works enumerated, leaving out those burning both pyrites and brimstone, or coal-brasses, or "oxide."

In the 20th Report, pp. 48 & 49, we find the average of 18 works burning pyrites to be 23·1 cubic feet of chamber-space (minimum 15·5, maximum 38·4); the average of 10 works burning brimstone 29·7 cubic feet (min. 21·7, max. 44·8). In the 21st Report, pp. 20 & 21, 21 works burning pyrites average 26·6 cubic feet (16–40); 15 works burning brimstone average 26·2 cubic feet (21–48). On pp. 64 & 65, 22 works burning pyrites average 29·2 cubic feet (17·3–43·2); 18 works burning brimstone average 31·4 cubic feet (19·3–46·2). But as the great majority of these

works are too small to afford a real guidance in this matter, we will quote in detail (from 21st Report, p. 81) the figures of fifteen medium and large-sized works in the Widnes district, comprising some other interesting information :—

Pyrites burnt per week. Tons.	Cubic feet cham- ber-space per lb. of S burnt in 24 hours.	Nitrate of soda per cent. of sulphur burnt.	Capacities of Gay- Lussac towers per ton pyrites used per week. Cub. ft.	Total Acidity of Waste Gases as grains SO ₂ per cub. ft.
175				
52	21.0	3.50
350	18.0	5.00	65.8	0.87
210	17.8	4.70	18.7	2.10
125	28.0	4.00	36.1	0.65
98	17.8	4.20	32.4	2.88
240	21.0	4.25	24.0	1.71
250	28.3	3.75	15.7	2.34
150	21.0	37.8	0.79
250	19.3	5.00	20.5	1.90
60	22.3	27.5	3.89
260	22.0	3.30	33.7	1.40
117	21.0	4.00	53.5	1.30
183	20.0	21.5	2.94
70	17.5	79.6	0.70
Totals and averages	2590	4.17	44.4	1.82

The usual proportions in the south of France are stated by Favre (Monit. Scient. 1876, p. 271) as follows. Each square metre of grate-surface in the pyrites-burners daily receives 270 kilograms of 40-per-cent. pyrites, and corresponds to 180 cubic metres of chamber-space. This means 1.66 cubic metre for each kilogram of sulphur charged, or 26.5 cubic feet per lb.

In the north of France I found, in 1878, about 8 cubic feet per lb. of pyrites, or about 17 cubic feet per lb. of sulphur charged, with good yields and low consumption of nitre, but only for low or medium temperatures; in summer $\frac{1}{4}$ to $\frac{1}{3}$ more chamber-space is required.

During the last few years a new style of working has been introduced into several French works as "*production intense*," say "forced work." It consists in supplying the chambers with a largely increased stock of nitre, without losing any of it, by means of largely increased Gay-Lussac and Glover towers; in this way the production may be increased to almost twice the usual amount, so that, in winter at least, a maximum of yield and a minimum

consumption of nitre is attained with the extremely small chamber-space of 0·7 cubic metre per kilogram, or 11·2 cubic feet per lb. of sulphur burnt. We shall have frequent occasion in later parts of this book to speak of this "forced style," which at the time of writing is nowhere practised in England or Germany.

Evidently the best proportion of chamber-space to the sulphur burnt cannot be fixed absolutely, but several conditions have to be taken into account. First of all, it is not indifferent whether rich or poor pyrites is used. The latter requires proportionally more air and furnishes poorer gas, and thus needs more chamber-space. At Oker each cubic metre of chamber-space yields 2·85 kilograms chamber-acid of 106° Tw. in the case of rich ores, but only 2·0 kilograms with poor ores. The first corresponds to 35·5, the latter to 48 cubic feet of chamber-space for each lb. of sulphur actually recovered in the vitriol. Furthermore it is very important with what temperature the gas enters the chambers. The better it is cooled, the less volume it occupies for equal weight and the less chamber-space is used. For this reason a Glover tower, which cools the gas very completely, causes, even from this reason alone, apart from others, a saving in chamber-space. It is also well known that in winter for the same chamber-space either a good deal more pyrites can be burnt or less nitre is consumed than in summer.

At some works the chamber-space is stated in so many cubic feet per ton of salt-cake made per week. Hurter gives the following useful rules for converting one kind of expression into another. Supposing the chamber-space is given in cubic feet per lb. of sulphur burnt in twenty-four hours, you will obtain the number of cubic feet per ton of salt-cake made in a week by multiplying with 75. Given, on the other hand, cubic metres per kilogram: by multiplying with 16 you express the result in cubic feet per lb. of sulphur, and by multiplying with 1200 you obtain the number of cubic feet per ton of salt-cake made per week.

Proposals for diminishing the chamber-space.

The considerable ground-space taken up by the ordinary vitriol-chambers, and the very large capital required for these immense leaden erections, on the Continent also the expense of the correspondingly vast buildings containing them, has led to a great many proposals for restricting the chamber-space, or for doing

away with lead chambers entirely and substituting cheaper apparatus for them. One way of greatly diminishing the space required for the reactions of the vitriol-making process would be to use *pure oxygen* instead of air for oxidizing the sulphur. This, indeed, forms the subject of patents by Terrell, Hogg, and Tomlinson (1871), and of A. & L. Q. Brin (E. P. 12,070, of 1886); also by Ellice Clark, as communication from G. Lunge (E. P. 3117, 1888) (comp. also Bode, in *Dingler's Journal*, v. 216, p. 453); but it is unlikely that by any mode of manufacture whatever will oxygen become cheap enough to serve for making ordinary sulphuric acid.

Nearly all other proposals for manufacturing sulphuric acid in a diminished space start upon the assumption that in the ordinary vast chambers the gases are not sufficiently well mixed; some of them also on the theory that there is not enough "condensing" surface for the sulphuric acid, and that this should be artificially increased. So far as it was assumed that the sulphuric acid required to be condensed from a vapour into a liquid, similar to the condensation in distilling alcohol, &c., this theory is, of course, wrong, inasmuch as the sulphuric acid is liquid as soon as formed, and does not exist at all in the chambers in the state of vapour. But we shall see further on that for other reasons it is certainly true that a large amount of *surface*, for the chamber-gases to impinge on, is indeed a most important factor in the chamber-process, and that, moreover, a certain amount of *cooling* is also of great importance in this respect. We shall see that this proceeds from the necessity of bringing about the reaction between the nitrososulphuric acid and the water or dilute sulphuric acid floating about in the chamber. Whilst, therefore, we must acknowledge that former inventors were on the right track when increasing the surfaces of contact, it is a fact that their efforts were unsuccessful; but this was caused by the fact that they chose the wrong means for their ends. Partitions within the chambers, if made of lead, are most quickly corroded; if made of glass, they soon collapse (*vide* p. 366).

An arrangement of Ward's (E. P. 1006, of 1861) consists in a kind of mixing-chamber, for the combustion of 7 tons pyrites in twenty-four hours, 64 feet long, 16 feet high, and 20 feet wide, followed by a second lead chamber, or flue, 200 feet long by 3 feet high and 3 feet wide, almost filled up with sheets of glass to a

length of 25 feet. The sheets lie in a horizontal position, and are kept a little apart by strips of glass, to permit the passage of the gases. Ward believed that upon these sheets (in lieu of which tubes might be used) nitrous vitriol would condense and afford a large surface to sulphurous acid. His plan does not appear to have been carried out in practice, or, if so, it must have been abandoned again, probably because his erection possessed too little stability or was too easily stopped up. The horizontal arrangement is also unfavourable to a systematic action of the gaseous and liquid agents, for which streams in opposite directions (up and down) are preferable, as we shall see below; and the total lack of a cooling arrangement would make the whole principle of reaction on the solid surfaces incomplete, as will be proved further on.

Mactear (Journ. Soc. Chem. Ind. 1884, p. 228) has carried out some experiments showing the importance of surface condensation. A tray, placed in a vitriol-chamber, one square foot area, was found to give 708 grammes H_2SO_4 in 24 hours. By placing in the tray 12 pieces of glass, 12 in. by 6 in. each, in a vertical position, the amount of acid obtained in 24 hours rose to 1644 gr., or 2.3 times as much, and by placing the glass slips horizontally, the same distance apart as before, the acid rose to 3226 gr., or 4.5 times more than without the glass. Other experiments made with "surface condensers" within the chambers showed that in the case of flat vertically placed sheets, the side facing the gaseous current condensed more acid than the opposite side, in the proportion of 100:78. When the same plates were placed horizontally, with their edges facing the current of the gases, the amount obtained from the double surface was 172, against 178 in the former case.

The principle of surface condensation is also employed in de Hemptinne's chamber-system, which will be mentioned in the 11th Chapter, in connection with his system of concentration.

A similar principle, in which, however, the idea of mixing the gases was the chief aim of the inventors, is involved in the proposal made by Gossage and many others, and frequently carried out in practice, of filling the chambers partially or entirely with *coke*, or of erecting special coke-towers at the end of the set, not as Gay-Lussac towers, but to be merely moistened by water or steam. In practice it has been found that even as a matter of

construction this plan gave much trouble, because the great weight pressing upon the outside layers of the coke makes it bulge out or even cut through the chamber-sides. But apart from that it was found that the yield of acid for a given chamber-space was *not* increased, that more nitre was used, and that the acid was made impure by the coke. Everywhere, therefore, the coke has been removed again from the chambers themselves, and has been relegated to its legitimate place in the Gay-Lussac tower. The cause of this failure is probably a twofold one: firstly, the injurious action of the coke on the nitrous gases, which would thereby be reduced with formation of carbonic acid (comp. close of Chapter IX.); secondly, the lack of any cooling, just as in Ward's case.

The same objections hold good for the apparatus of Verstraet (Bull. Soc. d'encourag. 1865, p. 531), which was worked in Paris for some time, but had to be given up as impracticable. It consisted of a number of stoneware jars without a bottom, covered 430 square feet of ground, cost only £280, and was to supply daily a ton of vitriol of 106° Tw. There were twelve perpendicular stacks of five jars each, filled with coke and traversed by the burner-gas; nitric acid ran down over one of them, meeting the sulphurous-acid gas; and the resulting acid was in regular rotation run over the other stacks.

The apparatus of Lardani and Susini (Bull. Soc. Chim. viii. p. 295) is founded on the same principle. Its peculiarity is a "reaction-apparatus," whose lower part is filled with sulphuric acid, on the top of which a thick layer of nitric acid is floating; the upper part, divided from the lower by a perforated partition, is filled with pumice; the nitre-gas is regenerated to nitric acid by an excess of air and water in a system of pipes filled with pumice or coke.

That mixing the gases alone is not sufficient is proved by the small success of Richter's apparatus (G. P. 15,252), consisting of a steam-injector on the top of the chamber which aspirates the gases from the lower part of the chamber and re-introduces them at the top. It is true that by this apparatus probably only a small portion of the gases would be set into circulation; otherwise the draught would have been interfered with in an intolerable way. At all events no great advantage has been obtained by using it in all the factories visited by me; but at some

places a certain improvement is said to have been produced thereby.

An attempt in this direction, which for a time roused great hopes of accomplishing its object, was the plan of Thyss (G. P. 30,211; Fischer's Jahresb. 1885, p. 216). We shall give some notes upon it from a detailed description given by myself in the 'Zeitschrift für angewandte Chemie,' 1889, p. 265, of a plant erected at Turin. Between each two chambers of a set there are interposed one or more lead columns $8 \times 2\frac{1}{2}$ feet wide and 12 feet high. They are filled with a number (25) of horizontal wooden frames, covered with lead, and so disposed that the gases must take a zigzag course in passing through the column (in the original patent these plates were perforated with many holes, but at Turin this had been given up as useless). The gas is introduced in the middle of the top, and is taken away at the bottom; as the draught is very much impeded by the 25 zigzag ways it has to take, there are steam-injectors both in the inlet and the outlet pipe. All other details are unessential, and only important for the special case described. In a prolonged practical trial it was found that the first column produced 7.3 times as much acid as an equal cube of ordinary chamber-space, the second and third 3.4 times, the last (behind the set) 1.2 times, the average 3.9 times as much. Leaving out the column at the end, which was evidently misplaced, the Thyss columns in that instance produced about 5 times as much acid per cubic foot of their contents as the ordinary chambers. Thyss himself asserted (without sufficient proof) that he had made 9.25 times as much acid in his own columns as in an equal cube of chambers. But even this is a very small matter if we consider the very great expenditure for lead incurred by that system. At Turin the four columns altogether contained 980 cubic feet, with a lead surface of about 5000 square feet. Supposing a maximum production of 10:1 against an ordinary chamber, the four columns would be equivalent to a small chamber of 9800 cubic feet capacity, which would require only 3500 superficial feet of lead against the 5000 feet in the Thyss columns. But the latter, requiring very complicated labour, would cost much more, at least equivalent to 7000 feet of ordinary chamber lead. Thus, even on the estimate of Thyss, his plan would cost twice as much, but according to the Turin experiences four times as much as ordinary vitriol-chambers.

This alone is of course more than sufficient to condemn that plan; but there is an even graver objection to it. Some of the towers were corroded within a few months, and would have had to be renewed if the process had been continued at all. It was, however, abandoned because, in spite of employing injectors, the draught was intolerably bad, the pyrites was incompletely burnt, and both the yield and the strength of the acid produced in the whole set of apparatus sank to an alarmingly low figure.

The causes of this complete breakdown of the Thyss plan are not far to seek. Even its constructive principles are wrong. We have had on more than one occasion to point out how quickly lead is corroded if it is exposed to hot chamber-gases without being outwardly cooled by air &c. In the present case it is intended to even intensify the reaction in a leaden column filled with sheets of lead entirely exposed on both sides to the action of the hot gases! In this respect the Thyss columns are even a considerable step behind Ward's chambers filled with sheets of glass (p. 375). Another fault in his system is this, that he brings nothing into play except contact with *hot* surfaces; but this, as we shall see, does *not* constitute the proper conditions for the mutual action of the agents, and thus it is no matter of surprise that his system fulfilled so few of the expectations connected therewith. But that, in spite of the mistake just pointed out, the Thyss columns do make much more acid than an equal space of ordinary lead chamber, certainly proves that even in that imperfect form an intimate mixture of the gases and their contact with solid surfaces are conducive to their mutual reaction.

Sorel (comp. Zeitsch. f. angew. Ch. 1889, p. 279) proposes making a first chamber of half the usual size; the gases then pass a number of cooling-tubes and then into two or three small columns, in which they travel upwards, together with steam, whilst a stream of sulphuric acid of 140° Tw. is running down. With three such columns 60 per cent. of the chamber-space is to be saved. Sorel's proposals are decidedly on the right track, but the details of construction are too little elaborated, and his plan of feeding the columns with acid of the same concentration as a Gay-Lussac tower seems altogether wrong, although he propounds a very ingenious theory for it. At all events he has not succeeded in getting his plan tried anywhere, although he was connected with one of the wealthiest and most enterprising chemical companies.

I have myself (Zeitsch. f. angew. Chemie, 1889, p. 385) endeavoured to combine all the principles hitherto recognized as paramount in the manufacture of sulphuric acid in the following way. In the 9th Chapter, when treating of the Theory of the Chamber Process, we shall see that it consists essentially in this: that nitrous acid (or anhydride), or in the first part of the chambers nitric oxide, acts as carrier of atmospheric oxygen and water upon sulphur dioxide, by which action nitrososulphuric acid is formed. This acid, which for the most part at once dissolves in the sulphuric acid already present, like this floats about in the chamber in the shape of a fine mist. When coming into contact with water, or, which is probably the usual case, with dilute sulphuric acid, a decomposition takes place by which the nitrososulphuric acid takes up water; sulphuric acid is now formed, and all the nitrous acid is returned into the atmosphere of the chamber to recommence the above-described action.

It is evident that all these reactions require in the first instance a most intimate and constantly renewed *mixture* of all the gases, vapours, and misty particles. In the ordinary large chambers a long way, a vast space, and a correspondingly long time are needed till the reactions are practically complete; that is, till nearly all the SO_2 has been removed from the gases. If it were only the question of a mixture of gases and vapours, probably very much less time and space would be required; but as both the nitrososulphuric acid and the dilute sulphuric acid, which are to act upon one another, are in the state of mist, that is, of minute liquid drops, they may travel for some distance side by side without coming into actual contact and reacting as they ought to do. In many similar cases it has been found that simply mixing up the atmosphere in question is nothing like so efficient as presenting large *solid surfaces* against which the gaseous current must strike in its progress. By the shock against these solid surfaces, and the loss of velocity thereby incurred, and undoubtedly also by surface attraction also, the misty particles which would otherwise float about for hours in the same state are condensed on those surfaces in larger drops or films, and then the mutual reaction above described, leading to the splitting up of nitrososulphuric acid, will take place at once. From this we infer that we ought to arrange a number of large solid surfaces in the path of the gaseous current, but so arrange them that this current must constantly

strike against them and be constantly broken up into small parts and mixed up again. (In this respect Ward's glass sheets, running parallel with the gaseous current, were not properly disposed.)

There is, however, another condition to be realized for a proper working of the chamber process. As we shall see further on, it is indispensable that the *temperature* of the chamber is kept sufficiently low to condense the requisite quantity of aqueous vapour into liquid water or dilute acid, sufficient for decomposing the nitrososulphuric acid. As the reactions going on within the chambers produce a large quantity of heat, the process cannot go on without a portion of that heat being abstracted again, which in the ordinary system is done by radiation from the chamber-sides. The separation of the whole chamber-space into several smaller chambers acts favourably in this respect, as the ends of the chambers and the connecting-pipes act as cooling surfaces; and Sorel (comp. above) actually proposed increasing this by arranging a set of cooling-pipes, which, however, would be nothing like sufficient for the purpose. My own plan is, however, different from anything formerly proposed. I effect the necessary lowering of the temperature, not by radiation or convection to the outer air, but from within by a shower of water or very dilute sulphuric acid. Thus several objects are attained at the same time. The temperature of the chamber atmosphere is reduced to a proper level, parts of its heat being spent in vaporizing water; but this water is just what is required for carrying on the chamber process itself, and thus a saving is effected in the raising of steam for the purpose of supplying the vitriol-chambers; we also supply this water in a finely divided form, and exactly where it is needed for meeting and decomposing the nitrososulphuric acid condensing on the solid surfaces; and by this cooling we protect the apparatus employed against rapid deterioration.

The apparatus actually employed by me is on the principle of the "Plate-column," invented by myself and patented with Ludwig Rohrmann, E.P. 10,355 of 1886; 10,037, 1887; 6989, 1889. It originally consisted of a column of large stoneware cylinders, filled with the plates forming the peculiarity of the invention; and this is the construction still employed for nitric and hydrochloric acid (p. 91); but for the purpose of sulphuric-acid manufacture it is constructed with a leaden shell (*a*) of either

Fig. 133.



Fig. 134.

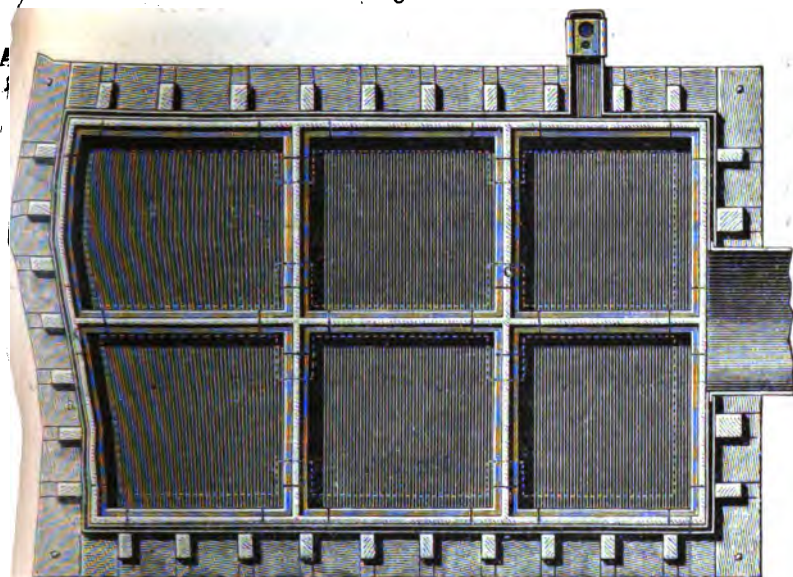
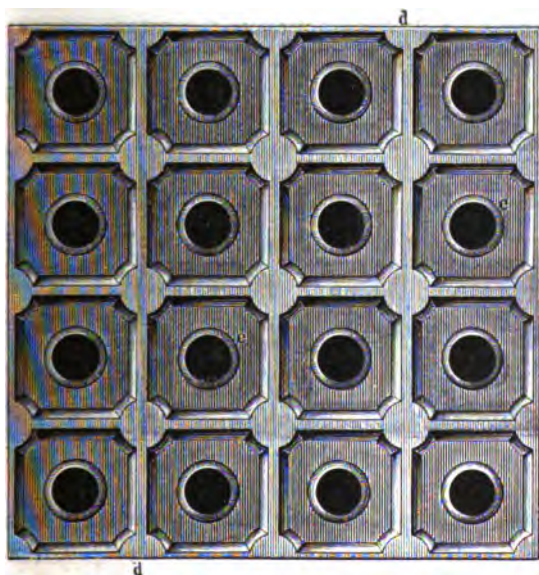
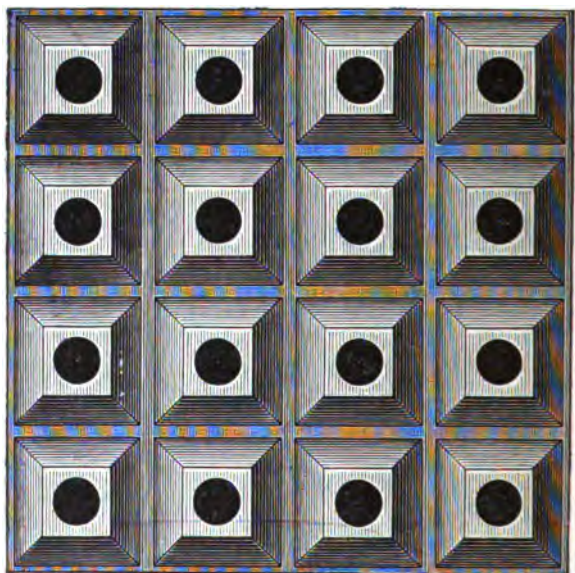


Fig. 135.



round or angular section, and stoneware plates (*b, b*), as shown in figs. 133 & 134. The plates are supported by bearers, *c, c*, in such a way that each plate is independent of the others, and presses only upon the horizontal ledge of its own bearer, whilst the pressure of the superposed plates and bearers is taken up by the vertical part of the bearers. The latter are easily arranged so as to protect the whole inner surface of the lead against the attack of the chemicals and the high temperature ruling within. We do not speak of such parts as the feeding-arrangements, inlet and outlet pipes, and the like, which require no special explanation; the feeding-arrangement will be described in the 8th Chapter, in connection with the Gay-Lussac tower. A special explanation is only necessary for the plates *b, b*. Fig. 135

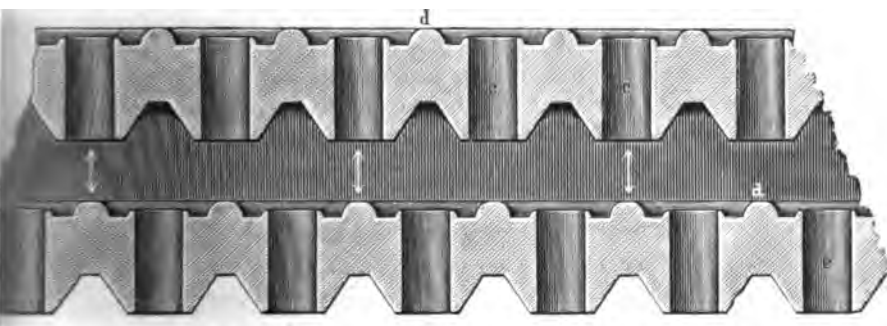
Fig. 136.



shows a small portion of their surface, as seen from the top, fig. 136 the same as seen from the bottom, fig. 137 a section of pieces of two superposed plates.

Each of these is covered with a network of small ledges, *d d*, and in each of the squares thus formed there is a perforation, *e, e*, with a somewhat raised margin. The height of this margin is not quite so great as that of the ledges, hence there is always a layer of liquid about $\frac{1}{8}$ inch deep in each of the squares, and as there is always more liquid dropping in, the excess is forced out through the perforations drop by drop. The plates are not identical in shape, but differ as to the position of the holes. To each perforation in any one plate there corresponds the point of union of the ledges in the plates above and below (see fig. 137). Hence the liquid cannot drop straight through the holes in the following plates, but strikes the solid portion of the next plate, is

Fig. 137.



scattered about, and is divided among the adjoining squares. This action is repeated from plate to plate. Thus the thin layer of liquid resting upon the plates and clinging to the holes is constantly renewed, and by the scattering about of the liquid another absorbing surface is created.

The gases and vapours rising within the column pass through the numerous holes of the lowermost plate and are thus divided into a great number of fine jets. Immediately on issuing through the holes of this plate, they strike against the solid places in the next plate above, which correspond to the holes, and are thus divided and mixed again; and this process is repeated as many times

as there are plates provided. Whilst the gases and vapours thus travel upwards in continuously renewed mixtures they come into the most intimate contact with the absorbing liquid, which they meet within the narrow holes on the plates and scattered all over in fine drops. By the incessant changes in the direction of the current, and the equally incessant renewal of the surface of the liquid, the most favourable conditions are produced for a mutual action of the gaseous and liquid substances. Owing to the principle of the apparatus, no false channels can exist in which the gases or liquids would travel separately without coming into proper contact with each other.

This circumstance partly accounts for the enormous difference in condensing-power between the "plate-column" and a perfectly well-constructed and packed coke-tower, or any similar apparatus, fitted with pieces of pottery and the like. The liquid within a coke-tower is never quite evenly distributed; there are always many places where it drops down a considerable height without meeting a piece of coke, and where, on the other hand, the gases find channels in which they can ascend without for some time getting mixed and coming into contact with liquid. Moreover, the individual gas-channels are too wide, and the inner portion of the gaseous current does not enter into reaction with the absorbing liquid. This is unavoidable, because the interstices between the pieces of coke are quite irregular, and therefore the section of the tower must be made wide enough and the pieces of coke large enough to secure a sufficiency of draught for the worst case. Nor, as experience has demonstrated, have any arrangements of pieces of pottery hitherto had a better effect than coke. Hence coke-towers must be made very wide and high, thus offering a long time and corresponding opportunities for mixing the gases and enabling them to come into contact with the liquid; and in this way the reaction is certainly very complete at the end. But this enormous enlargement of space can be avoided by the systematic way in which, in the plate-column, the gaseous current is split up into upwards of a thousand very thin and exactly equal jets, which must continually alter their direction, and must therefore become thoroughly mixed each time they pass through a new plate. On their way they come into the most intimate contact with constantly and systematically renewed thin layers of liquid. The network of ledges prevents any unequal downward passage of the

liquid, unlike the action of coke-towers or of any other hitherto known form of similar apparatus. Perhaps a still more important difference is the following :—There is a very thin and constantly renewed layer of liquid standing on each plate, and the gases, in passing through the perforations of the plate, must frequently break through the drops of liquid. This seems to produce an action somewhat similar to the Coffey still or other “rectifying” apparatus, and it may to a great extent explain why such an intense action takes place in so small a space.

Owing to these advantages a plate-column, in comparison with a coke-tower, does from ten to twenty times as much work in the same cubic space. It can therefore be made not merely much smaller in section, but also much lower in height, and the feeding-liquid requires correspondingly less pumping. A column of 40 plates would be only 18 feet high. The above is a comparison between plate-columns and coke-towers; the difference between the former and empty chamber-space is much greater, as we shall see.

In our present case it is of special importance that the injurious action exerted by the reducing power of coke upon the nitrous gases (p. 160) is avoided, the stoneware plates being absolutely stable in the chamber atmosphere if manufactured in proper quality. The plates, therefore, last for ever; even if cracked they may still continue in use.

When a plate-column is partly obstructed by muddy deposits, it is very easily cleaned out by a thorough flushing with water, or, in bad cases, by removing the cover and lifting out one plate after another.

Apart from the great constructive difference between the plate-columns and all previously proposed apparatus, there is an equally great difference in their mode of application. If the column were left to itself, like Ward's or Thyss's apparatus, the very completeness of the mixture produced therein would produce an intense chemical reaction, and, consequently, a very injurious development of heat. This is, however, entirely avoided by feeding the columns with a stream of water or very dilute sulphuric acid, at such a rate that, by the vaporization of water, the temperature does not rise above 70° or 80°. The intimate contact between gaseous and liquid particles within the plate-column must bring out the cooling action of the evaporation of water to its fullest

extent, and at the same time the water required for the chemical reactions of the vitriol-making process is supplied here without any previous production of steam or spray; the superfluous steam passes over into the next chamber, and does its work there. The acid running off at the bottom is either used up as it is, or is run into one of the chambers, or it is employed for feeding the Gay-Lussac tower.

In plate-columns there will always be a great excess of nitrous gas and of oxygen; hence there is very little fear that even when employing water for feeding them there will be the conditions present for the formation of nitrous oxide, which would mean a waste of nitre. This could be avoided in any case by feeding the columns with dilute acid up to 1.3 spec. grav., since I have previously shown (*Ber. d. deutsch. Chem. Ges.* 1881, p. 2200) that in this case no N_2O whatever is formed. But this will hardly be necessary: when feeding with water, on the top plates some nitric acid will be formed which in its downward course is soon reduced to nitroso-sulphuric acid, and this itself is lower down denitrated, and runs off at the bottom as chamber-acid.

The principal advantage of this system is that, like the Glover tower, it brings about the mutual action of the ingredients within the smallest possible space. We shall see in Chapter VIII. that one cubic foot space in the Glover tower effects the formation of as much acid as at least 180 cubic feet of ordinary chamber-space; and a similar difference may be looked for between the latter and the plate-columns to be interposed between the chambers.

We will now go into the question whether the thermal effects produced in that system are not excessively large or small. The heat of forming H_2SO_4 from $SO_2 + O + H_2O$ is 54,400 calories; to this must be added the heat produced in the formation of ordinary chamber-acid, say, of 110° Twaddell, or $H_2SO_4, 3 H_2O = 11,100$ calories; altogether 65,500 calories. This is the heat produced in the formation of a quantity of chamber-acid corresponding to 98 grams of H_2SO_4 , and it is very little more than would be required for converting 98 grams of cold water into steam. This quantity of water then would have to be evaporated within the column in order to absorb all the heat produced in the vitriol-forming process, on condition that the acid must run

out cold at the bottom and that the column would lose no heat by radiation. But as the former condition is unnecessary, and the latter even impossible to maintain, the quantity of water evaporated will be less than the weight of monohydrate produced, and will probably be very nearly equal to that required for the chamber-process, viz. three quarters of that amount. Any deficiency of water could, of course, be made up by steam, probably best in the shape of an injector placed in the outlet tube from the plate-column.

The most practical way of applying the new system would be as follows:—Considering that by far the greatest portion of the acid is made in the first part of the chamber, we cut off the back part altogether, and leave behind the Glover tower a chamber of only about 50 feet length. Behind this we place a plate-column of sufficient section for the amount of gas to pass through and 40 plates high (say 18 feet). Then comes a small chamber, say 30 feet long, again a plate-column, a last chamber for drying the gases, and in the end a plate-column serving as Gay-Lussac tower.

The question might be raised why we do not propose to carry on the whole of the vitriol-making process in plate-columns or similar apparatus. But a glance at the curves shown in the 7th Chapter will show that the first part of the first chamber is really very efficient, and whilst the gases are of such concentration a lead chamber will be the cheapest apparatus for making sulphuric acid. As soon as the curve is beginning to bend towards the horizontal, that is, when the reactions become sluggish, it is time to liven them up by apparatus like the plate-columns. But if such were attempted to be used from the first, the heat would become excessive, which would be very injurious both to the material of the apparatus and to the process. For this reason the process proposed by Hannay (E.P. 12247, of 1886, comp. Chap. XVI.) is not likely to be practically successful.

The apparatus for absorbing gases by liquids, patented by Hoffmann and Carlisle (G.P. 48283), is shown in figs. 138 & 139. It is a column or tower, fitted with groups of spouts, *a a*, inclined in opposite directions, in connection with overflow vessels *b b*. This apparatus is also intended to make sulphuric acid from sulphur "evaporating" at the same time with nitric acid, both of them being forced into the apparatus by an injector, while the "spent gases" are forced back by another injector into the sulphur

chamber. It is not stated what material this apparatus is to be made of, and the very curious proposal for making sulphuric acid last described will suffice for judging of its technical value.

Fig. 138.

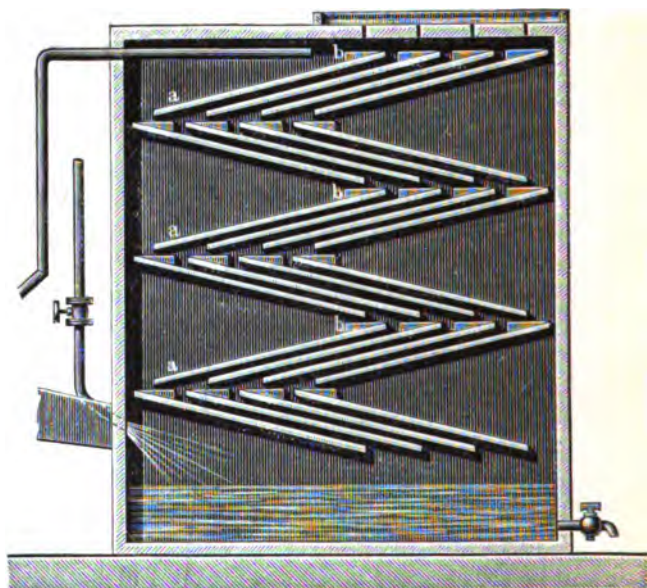
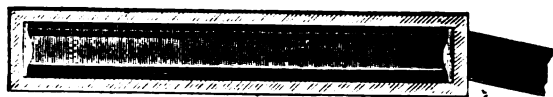


Fig. 139.



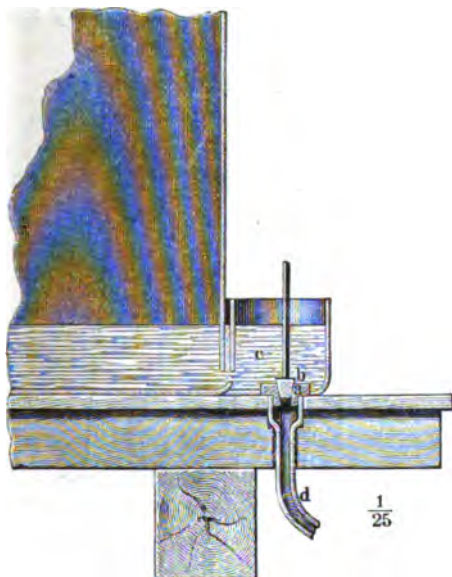
Chamber-fittings.

Each set of chambers must contain a number of auxiliary apparatus, which in part are absolutely necessary for the process, in part serve to check it chemically and technically: the former are essentially those for introducing the nitre, the steam, and the air; the latter, smaller apparatus shall be described first.

Drawing-off the acid is never done by cocks attached to the chambers, which might be made of hard lead (4 to 5 Pb to 1 Sb);

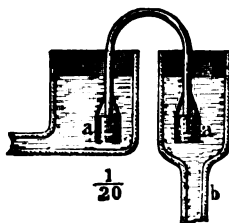
but they would readily get stopped up with sulphate of lead, and could not very easily be repaired when leaking. It is best to put beside a chamber a round or square lead box, open at the top, of the same height as the upstand of the chamber-bottom, and connected at or near the bottom by a wide pipe with the chamber; or a suitable piece may be burnt on to the chamber, as shown in fig. 140, and the connection made by a slit. The box may be

Fig. 140.



provided with a stopcock; but more usually, as shown in the figure, it carries in its bottom a valve-seat *a* of regulus metal, into which fits a conical plug *b* of the same metal provided with an iron handle covered with lead. The running-off pipe *d* is either burnt to the valve-seat or joined to it by an open funnel; the latter permits the running-off to be more easily observed, but is apt to occasion running over, by getting stopped up. Or, as shown in fig. 141, a lead siphon may be employed, to which at the bottom two cups, *a a*, are joined, which always keep it filled, so that it begins to act

Fig. 141.

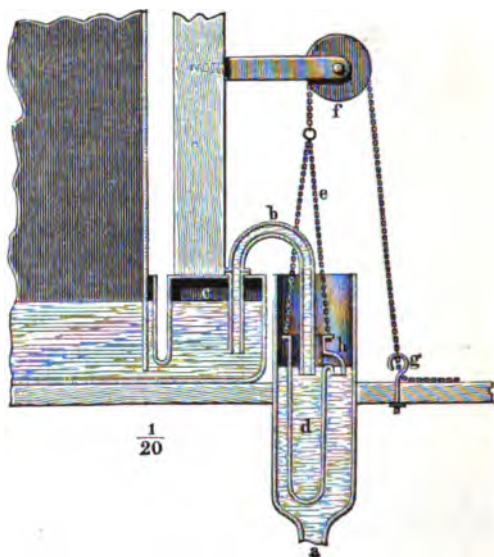


as soon as one of its limbs has been put into the acid. The second limb then enters into a large funnel of the running-off pipe *b*.

The simplest plan, which does not at all work badly, is this: to burn a short piece of thick lead pipe to the chamber side, and make the joint very strong by casting lead round it. This pipe ends over the funnel of the running-away pipe, and is closed by a good india-rubber cork. The men take this out and put it in by hand, with a bucket of water standing by to wash the acid off their hands.

The arrangement shown in fig. 142 is a very good one. The

Fig. 142.

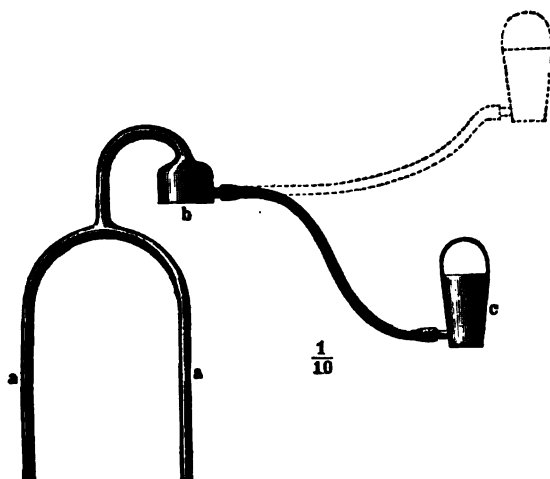


siphon *b* is firmly attached to the box *c*, or within the upstand of the chamber. A cylinder *d*, surrounding the outer limb of the siphon, is so suspended that it can be drawn up or down by means of the chain *e* and the pulley *f*, and fixed in any position by the hook *g*. The cylinder *d* forms a continuation of the outer limb of *b*; when it is quite drawn up, so that its overflow *h* is at a higher level than the acid in *c*, it will cease to run; but when *h* gets below this level, the siphon will at once begin to act, and the more quickly the

more *d* is lowered. Thus the acid can be run off with more or less speed and with the utmost cleanliness.

Fig. 143 represents a siphon suitable for hot acids in any part of the works. To the top of the siphon *a a* there is joined by a bent tube a closed lead vessel *b*, which by an elastic tube is connected with the open vessel *c*. The latter is filled with acid and lifted

Fig. 143.



into the dotted position, whereupon *b* and then the siphon *a* are filled; *c* is then lowered, whereupon the siphon begins to act, some acid running back from *b* to *c* and thus producing a partial vacuum.

We shall in this place also mention the best arrangements for inserting siphons into glass carboys or other vessels for carrying corrosive liquids. The simplest and most efficient plan is that shown in fig. 144. A glass or lead siphon, *a*, is put into a good india-rubber cork, made strongly conical so as to fit into bottles of very unequally sized necks; another short tube, *b*, passes through the same cork. The siphon, *a*, may or may not be provided with a tap, *c*. It will be seen without explanation that the siphon can be started by blowing into *b*. The flow of liquid may be stopped, either by closing the tap *c*, or, if there is no tap, by lifting out the cork, or by opening a third hole, provided in the cork for this

purpose. In the (very frequent) case of the mouth of the carbonyl being too irregularly shaped for the cork to fit air-tight, the remaining air-channels are stopped up with damp clay; and in an emergency a lump of damp clay may replace the india-rubber cork entirely.

Fig. 144.



Bode and Wimpf's siphon (G. P. 23794, Chem. Zeit. 1885, p. 907; J. Soc. Chem. Ind. 1885, p. 484; further improvements in Zeitsch. f. angew. Ch. 1889, p. 522) rests on a very similar principle, with addition of a ball-valve for stopping and starting the siphon. It seems to be specially adapted for nitric acid.

Alisch (G. P. 9133), Landel (G. P. 9307), J. P. y More (G. P. 28721), Opländer (G. P. 30662), and others have constructed different kinds of siphons.

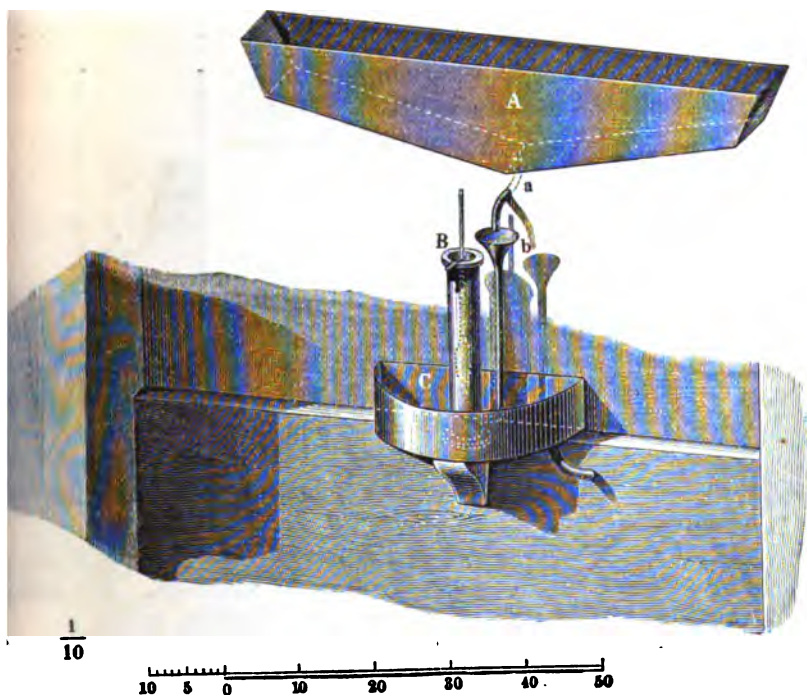
De Hemptinne has written a pamphlet, in which he traces great many forms of siphons to their authors; but there is nothing specially new in it.

J. Cortin, of Newcastle-upon-Tyne, makes *non-rotative acid valves* of a special mixture of regulus metal, the plug rising on

falling into its seat out of a mixed setting without turning round, so that it is free from friction in working, and the wear and tear is reduced to a minimum.

Acid-dishes (drips) are placed inside the chambers, in order to examine the process by ascertaining the quantity, strength, and nitrosity of the condensing acid. They are made in very different ways—for instance, that shown in fig. 145. A is a lead vessel, burnt against the chamber-side about 3 feet above the bottom. The acid caught here runs by the tube *a* through the chamber-side into the lead cylinder B, containing a hydrometer. B is provided near its bottom with a side-branch, *b*, reaching above its top, and ending in a funnel for receiving the acid, which thus constantly runs in at the bottom and out of the top of B into a vessel C, from which it is carried back by a small pipe into the chamber. The greater the length of A, the quicker the acid will be renewed in B, and the more reliable are the indications.

Fig. 145.



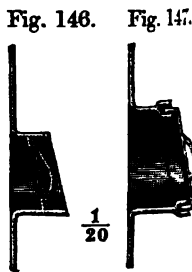
Many manufacturers have S-shaped drip-tubes in the connection between the chambers, for a similar purpose. Many others do not trust to the collectors burnt to the chamber-sides, but place leaden or stoneware dishes at some distance from the side within the chamber. These rest on feet made of lead tubes, or upon a stand of stoneware, so as to be elevated above the level of the acid; and they have an outlet leading outside the chamber. In some works, for instance at Aussig, both kinds of drips are fixed side by side; and it is noticed that those fixed to the sides always yield acid of 6° to 10° Twaddell less than the inner drips, evidently because on the sides more aqueous vapour is condensed along with the sulphuric acid.

For taking samples of the bottom-acid itself there is usually a recess made in some part of the chamber by dressing back the lower part of the side. Some, in order to be quite sure, always take the sample out of the chamber itself through a special small man-hole luted with moist clay; in this case there is a small loss of gas, but no danger of getting stagnant acid. Such a man-hole is shown in fig. 146 in section. The large *man-holes* may be made in exactly the same way; or else their lids may fit into a groove luted with damp clay, as shown in fig. 147. Large chambers are fitted with several acid-drips, man-holes, &c.

For taking the samples themselves a dipper of lead or glass is employed, which is lowered slowly, so as to get all layers of the acid into it. There is often a great difference between the top- and bottom-acid.

In German works there are regularly *thermometers* fixed about every 30 to 50 feet of the length of a chamber, whose mercury-vessel is inside, and whose scale is outside the chamber. This means of observing the temperature is undoubtedly infinitely better than the rough one commonly used in England, by touch of hand.

For chambers not exceeding 100 feet in length, one set of drops, thermometers, &c., is generally thought sufficient. For longer chambers this is not the case; at the German works there is generally a special set of these fittings for about every 60 feet length of chamber.

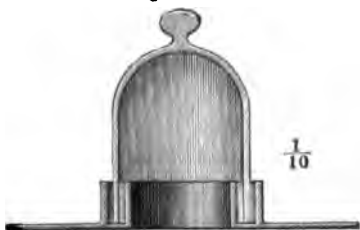


The *pressure* inside the chambers might be indicated by any of the anemometers, to be described further on; but usually simpler means are employed, such as simple glass pressure-gauges.

Sometimes clay plugs are put into holes made in the chamber-sides, in order to indicate the pressure inside the chamber. The tension of the gas is also seen by lifting the lids of the small man-holes (fig. 148), which are always made on the top of the chambers, with hydraulic lutes, and which generally consist of glass jars, so as to give light for observation through the side-windows (see below.)

A very sensitive pressure-gauge has been described by Vogt (Journ. f. prakt.Chem. xiv. p.284). The pressure is observed by the movement of a small

Fig. 148.

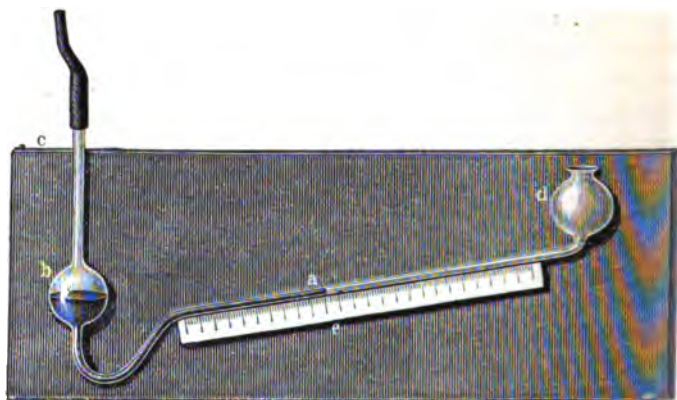


air-bubble playing in a horizontal glass tube of 4 or 5 millimetres diameter. The glass tube, apart from this bubble, is filled with water or another liquid, and is connected on each side with a bottle tubulated near the bottom. One of these bottles is 15 to 16 centims., the other 6 to 8 centims. wide; the liquid stands at the same level in both. The pressure within the lead chamber is made to act upon the surface of the liquid in one of the bottles, and its amount measured by the place of the air-bubble. The apparatus is all the more sensitive the greater the difference between the diameter of the tube and those of the bottles. There is a contrivance for admitting a bubble of air previously to using the apparatus, and for again equalizing the levels after use.

A very simple pressure-gauge, quite sufficiently sensitive for ordinary purposes, is shown in fig. 149 (from Sorel, Industries Chimiques, p. 142). The tube *a* has an inclination from the level in the proportion of 1 : 10; it is connected with a reservoir *b*, 1½ or 2 inches wide, upon which the pressure is brought to act by the elastic tube *c* (if there is suction, the vessel to be tested must be connected with the bulb *d*). The gauge is filled with a mixture of water and spirit of wine coloured by magenta or otherwise. As the movement of the liquid in the bulb *b* can be neglected, any movement of the liquid in the tube *a*, as measured on the scale *e*, corresponds to one tenth of its extent in real height. If, for instance, each degree on the scale is = $\frac{1}{10}$ inch, it indicates a

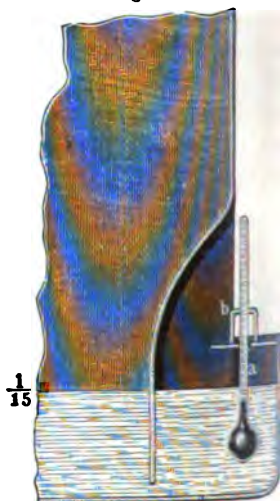
real pressure of $\frac{1}{100}$ inch. It is best to cause the liquid to move before each observation, in order to counteract the effect of friction within the tube.

Fig. 149.



For *gauging the height of the acid* there are either stationary lead gauges (which, however, are difficult to read-off exactly), or accurately divided copper rods, which are dipped in every time, but always in the same place, since the chambers are never absolutely level, or glass floats like that shown in fig. 150, the stem, *a*, of which slides in a small lead frame, *b*, whose upper edge serves as an index for reading-off. The float will sink more or less in the acid, according to any alterations in its specific gravity. To make this cause of inaccuracy less sensible, the ball of the float is made pretty large. The floats are the most convenient for reading-off.

Fig. 150.



A very important assistance in judging of the chamber-process is afforded by *glass windows* or *sights*, which permit the colour inside the chambers to be observed. Whoever has once got used

to them will never do without them again. These windows are 8 or 9 inches square, and are placed, at a convenient height for looking, in those places in the chamber-side which lie in a line with the glass man-hole lids in the chamber-tops; thus they are sufficiently lighted. Where the chambers are roofed in, light must be procured in some other way (for instance, by two opposite windows corresponding with a window in the chamber-shed, &c.). The chamber-glasses are put into small lead rabbets, and luted with white lead and boiled oil. Sometimes the assertion is made that the colour of the gaseous mixture, looked at across the width of the chamber, or in the diagonal line from the side to the man-hole lid in the top, is too deep, and that "sights" in the connecting-tubes are preferable; but just the opposite is the case, since the observations are evidently far more accurate, and any alterations of colour much more easily perceived, in the former than in the latter case. Only in the first part is the gaseous mixture, through copious condensation of acid, too opaque for observing its colour; but just there it is quite unnecessary, for only in the back parts of the set is it important to have always an excess of red vapours.

At some works they prefer to the ordinary side-windows, which are rather difficult to keep clean, glass jars, like those shown in fig. 148, p. 397, but placed on special short, wide branch-tubes, fused in the sides of the chambers at convenient places. These jars, if dirty, can be exchanged in a moment for clean ones, and they are supposed to show all the changes in the chamber-atmosphere, as well as the glass panes fixed in the lead-walls themselves; but my experience is decidedly to the contrary, as sometimes the side-jars are quite yellow while the chambers are already pale, and *vice versa*.

Apparatus for introducing Nitric Acid into the Chambers.

These are divided into two classes, according to whether nitric acid enters the chambers in a *gaseous* form, mixed with the burner-gas, whose heat evolves it from a mixture of sodium nitrate and sulphuric acid, or whether it is made in a *liquid* form in special apparatus, and introduced as such into the chambers. Opinions still differ on the point, which of the two plans is best. The plan of introducing gaseous acid, which is quite general in England, but only rarely used on the Continent, has the advantage of greater simplicity and of saving labour and fuel. The advantage

sometimes claimed for it of smaller loss than by making in the first instance liquid nitric acid, is hardly a real one; for some nitric acid is easily condensed during the conveyance of the gas to the chambers, and may corrode brickwork, iron, &c., whilst liquid nitric acid is always introduced exactly in the place where it is needed. The presence of nitric acid in the burner-gas will also induce a premature formation of sulphuric acid in the same, especially if it be much cooled; but the Glover tower obviates any inconvenience arising from this. On the other hand, some are afraid that the nitre-ovens may get so hot that a portion of the nitric acid will be decomposed down to NO or even to N; but mostly the men employ so much sulphuric acid for decomposing the nitre, that this cannot easily happen, nor are NO and N formed so very readily as was formerly apprehended (see below).

The advantages of introducing nitric acid in the *liquid* form are the following:—avoiding the entrance of false air into the chambers and the escape of burner-gas into the atmosphere, both of which occur in many (not all) systems of employment of gaseous acid; the possibility of employing as much nitric acid and as quickly as desired, whilst in the other case this depends on the heat of the burner-gas, which during a bad process, just when most nitric acid is needed, proves insufficient; lastly, and most of all, the exact regulation possible with liquid nitric acid, and its continuous supply, whilst gaseous acid is always given off from the nitre-mixture very unequally. These advantages have induced the great majority of continental manufacturers to adopt liquid nitric acid. Muspratt ('Dictionary of Chemistry,' ii. p. 1029) reports that a continental manufacturer, who previously worked with liquid nitric acid, after having seen the use of solid nitre in England, had saved one third of his nitre by introducing the English plan. This simply proves that that manufacturer had not been very careful before, and is no rule of action whatever. The opposite observation has been much more frequent. Liquid nitric acid, however, will do harm if the apparatus for introducing it is not constructed in such a way as to completely volatilize it or convert it into gaseous products before it reaches the chamber-bottom, since it will act upon this. Accordingly, sulphurous and aqueous vapour, which decompose the nitric acid, must be brought into as complete contact with it as possible.

In very large works the employment of solid nitre has this

advantage, that the chambers are not exposed to the damage possible with incautious handling of nitric acid, whilst, on the other hand, the irregular evolution of gas from the nitre-mixture is equalized by employing several decomposing apparatus, and charging them by turns, say, once every hour, just after a fresh pyrites-burner has been charged ; thus the stronger evolution of nitre-gas runs parallel with that of sulphurous acid. Still better is a contrivance for supplying gradually, and not all at once, the sulphuric acid serving for decomposing the nitre. It is contended that the best English works, all of which employ solid nitre, work with as small a consumption of it and as good a yield of vitriol as the best of the continental works employing liquid nitric acid ; also on the Continent, some manufacturers work quite as well with solid nitre as their neighbours with nitric acid ; but it is extremely difficult to check such statements, as few manufacturers lay open their *real* working results to outsiders, and, moreover, very many of them do not even know these results themselves with that degree of accuracy which would be required to decide this question.

There is no doubt whatever that the chamber-process can be worked more regularly by the continuous supply of nitric acid in the liquid form (comp. Eschellmann's experiments at Widnes, Chap. VII.) ; and the just objection to this, formerly existing, that there was a risk of damaging the first chamber in case of a collapse of the "cascades" (see below) has been entirely removed, in the first place by the almost general plan of introducing the nitric acid into the Glover tower, in the second instance by spray-producers &c. The labour of making nitric acid in large apparatus and condensing it in receivers is not much greater than that of frequent "potting" on the English plan ; the waste of sulphuric acid for decomposing the nitrate of soda is much less in the former than in the latter case, in spite of utilizing the nitre-cake, which pays for the coal consumed in manufacturing nitric acid. The nitric-acid retorts are even sometimes heated by pyrites-burner gases. These reasons explain why the majority of Continental manufacturers prefer the employment of liquid nitric acid for the chamber-process, in spite of the somewhat greater "trouble" involved, which, however, is more apparent than real. If all the trouble caused by the English potting-process, in producing a nuisance, running over of the mixture into the kilns, occasional bad decomposition of the nitre, frequent introduction of an

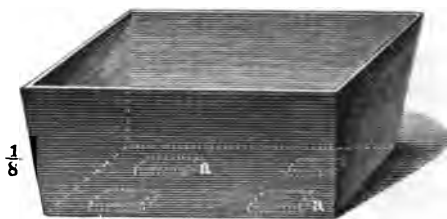
excess of air into the chambers, &c., were summed up, it would greatly exceed that involved in making and supplying liquid nitric acid. There remains hardly anything in favour of the English plan except the force of habit, and the fear of having some trouble in the transition from one mode of working to the other. That the imperfection of the present plan is felt even in England is proved by the various attempts at feeding the chambers with a solution of sodium nitrate, which are irrational in principle and have necessarily failed (see below).

We shall now describe both ways of introducing nitric acid, and begin with the

Introduction of Solid Nitre.

The apparatus serving for this has been partially described in a former chapter, along with the sulphur- and pyrites-burners. The drawbacks have been pointed out which attend placing the nitre-pots within the burners, or, generally, in such a way that the acid sulphate boiling over can run into the burners. Accordingly, recently there has always been a special *nitre-oven* constructed by enlarging a suitable place in the gas-flue. It is situated either above or, preferably, just behind the burners, and provided with the necessary working-doors and a cast-iron saucer for collecting what boils over. The nitre-pots themselves have various shapes—for instance, that shown in fig. 151; at *aa* ledges are cast on the bottom.

Fig. 151.



which facilitate pushing the pots backwards and forwards. They hold from 8 to 12 lb. of nitre.

The "potting" with these pots, which, strange to say, are still met with in some English works otherwise abreast of the times, is

very troublesome and imperfect. During the emptying and re-filling of the pots the doors of the nitre-oven are wide open, which does even more harm than in the case of the burners. The heavy pots, along with their melted contents, have to be taken up with long fork-shaped tools and emptied, which requires great strength and skill. The pots, freshly charged with nitre, are placed just within the door of the oven; the necessary acid is poured in from a jug by superficial estimation, and the pot pushed into its place; not till then can the door be closed. If the draught is good, a great deal of air must enter, meeting not even the same resistance as in the burners; if it is not very strong, which will more usually be the case, so much gas escapes that it can be smelled for some distance. Special dampers would partly obviate this, but are rarely met with. (Such dampers are mentioned in the official

Fig. 152.

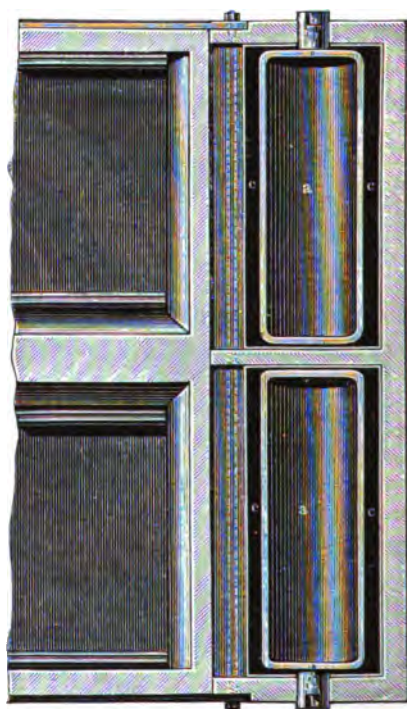


Belgian Report of 1855, p. 23.) The pots are quickly worn out, and must be replaced, especially if chamber-acid is employed in them. They last much longer if acid of 140° Tw. is used in them.

A much more perfect plan is that of decomposing the nitre in a

fixed apparatus, and running off the acid sulphate (nitre-cake) in a liquid form. This consists of a semicylinder of cast iron, *a* (figs. 152 & 153), with a cast-on tube *b*, bored somewhat conically. The latter projects out of the nitre-oven, and during the working is closed by a ground-in iron plug with a long handle. Outside there is a cast-iron saucer for holding the nitre-cake, which at once solidifies. The internal saucer, *c*, catches the boilings-over. The nitre is introduced by the hopper, *d*, which is provided with a damper; and after putting in the damper again, it is made gas-tight by filling

Fig. 153.

Scale $\frac{1}{38}$.

up with the next charge of nitre. An S-shaped tube (not shown in the diagram) serves for running in the vitriol, for which it is best to provide a small tank with a siphon or stopcock. The vitriol ought to be run out of this tank by a pipe with a very fine point into the S-shaped pipe, so that the running shall take a long time, and the nitre be only gradually decomposed. Sometimes an iron

scraper with a long handle (passing through one of the ends of the oven) serves for stirring up the mixture in the pan. The hole for this must be kept air-tight with clay. An apparatus of the size drawn here holds 56 lb. of nitre, which can be easily decomposed in two hours. In any case there should be two or more of these apparatus, so as to make the current of nitre-gas more regular by charging them in turns.

Even preferable to the arrangement here drawn is that of placing the nitre-trough in such a way that the burner-gas can play round the bottom as well. The saucer for the boiling-over stuff, which forms the bottom of the nitre-oven, must then be placed somewhat lower.

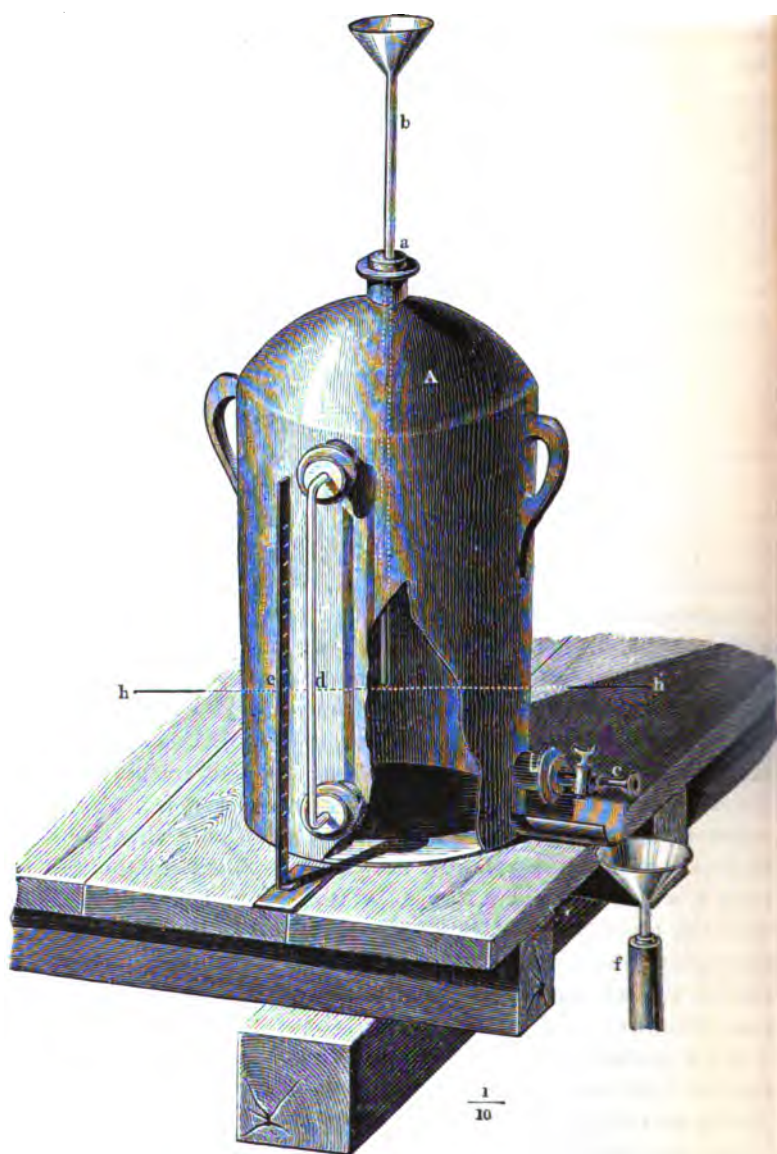
Introduction of Liquid Nitric Acid.

The nitric acid is employed of such strength as is obtained without difficulty from the above-described retorts.

It is of the greatest importance for the process to supply the acid in an even, continuous way, and to regulate the supply to a nicety. This can be done most simply by a Mariotte's vessel, as shown in fig. 154 on a scale of $\frac{1}{10}$. The stoneware vessel, *A*, containing the nitric acid, is closed by a caoutchouc cork, *a*, holding a glass tube, *b*. The latter is the only channel for the air which must take the place of any acid running out through the cock, *c*. As the liquid above the level *h h'*, down to which the tube *b* reaches, is supported by atmospheric pressure, only the height of acid below this can influence the speed of outflow; and this remains constant till the level of the acid has sunk below this point. The glass water-gauge, *d*, and the lead scale, *e*, admit of observing the height of liquid within the vessel. The latter is filled up through the tube *b*, which ends in a funnel at the top. During this either the cork must be raised, or it must be provided with a separate open glass tube which at other times is kept closed. The funnel *f* carries the acid into the glass or stoneware pipes conveying it into the chambers.

At some works there are two tanks which are filled up in turn, one of them every 12 hours, or both of them every 24 hours. The acid is running continually out of both. When one of them is half empty, the other one is just full; and thus the variation of pressure is compensated to a certain extent; but this plan cannot at all vie in regularity with a Mariotte's bottle.

Fig. 154.



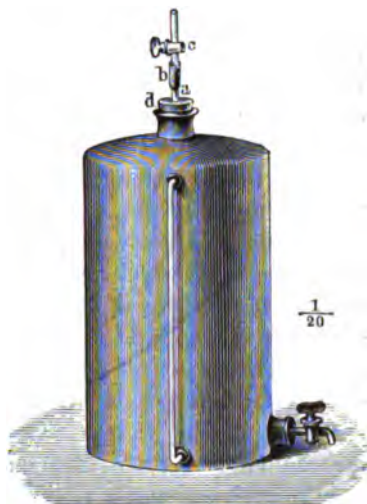
10 0 10 20 30 40 50 centimetres.

The Mariotte bottles sometimes get stopped up by grains of sand &c. getting into the slightly opened stopcock. Bode (Dingl. Journ. vol. 220. p. 538) avoids this by opening the cock full bore, stopping the neck of the bottle tightly by a caoutchouc cork (as shown in fig. 155), through which a tube, *a*, goes down to the desired depth, the latter being connected by the elastic tube *b* with a metal or glass cock, *c*, of $\frac{1}{8}$ inch bore, which serves for regulating the supply. Further improvements in this apparatus have been made by Liebig (Post's Zeitschr. f. d. chem. Grossgew. 1878, part 2).

Formerly the nitric acid used to be decomposed in one or two "tambours" (that is, small lead chambers) about $22 \times 10 \times 12$ feet, or cylinders of 10 to 13 feet diameter and 12 feet height, placed between the burners and the main chamber. The second of these contained the "cascades" or other spreading-apparatus; it stood at a higher level than the first tambour, into which it emptied its acid, and which only served for further exposing it to sulphurous acid, and completely driving off the nitrogen oxides. This first chamber received enough steam to prevent the formation of chamber-crystals, or to decompose them if they arrived in solution from the second chamber; the acid collecting in the first small chamber ran away into the main chamber. The first tambour is unnecessary; with proper regulation the nitric acid can be completely decomposed in the first apparatus by means of SO_2 and steam; but the latter ought to be supplied to such an extent that the sulphuric acid formed contains rather more than four molecules of water to each molecule of acid. At some French works the above-described faulty arrangement of the cascades caused the acid in the second tambour to contain a good deal of nitric acid.

The tambours have been mostly abolished, and the process is carried on in the main chamber; where the nitric acid, as is now

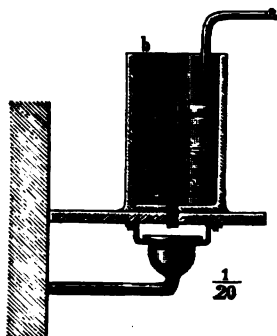
Fig. 155.



usual, is introduced through the Glover tower, the tambours are entirely unnecessary.

Some manufacturers prefer to run the acid not continuously in a very small jet, but intermittently in larger quantities. For this, nearly always, a siphon arrangement is employed (fig. 156). *a* conveys nitric acid into the stoneware vessel *b*; through its bottom passes a tube reaching about three fourths up its height, and open at both ends. This is covered by the wider tube *d*, which is closed at the top and open at the bottom, so that the acid fills up the space between the inner tube and *d*. As soon as it has got to the top of the former, this, along with *d*, forms a siphon which almost directly empties the contents of *d*, whereupon this is slowly filled till the acid has again risen to the top of the inner tube, and so forth.

Fig. 156.

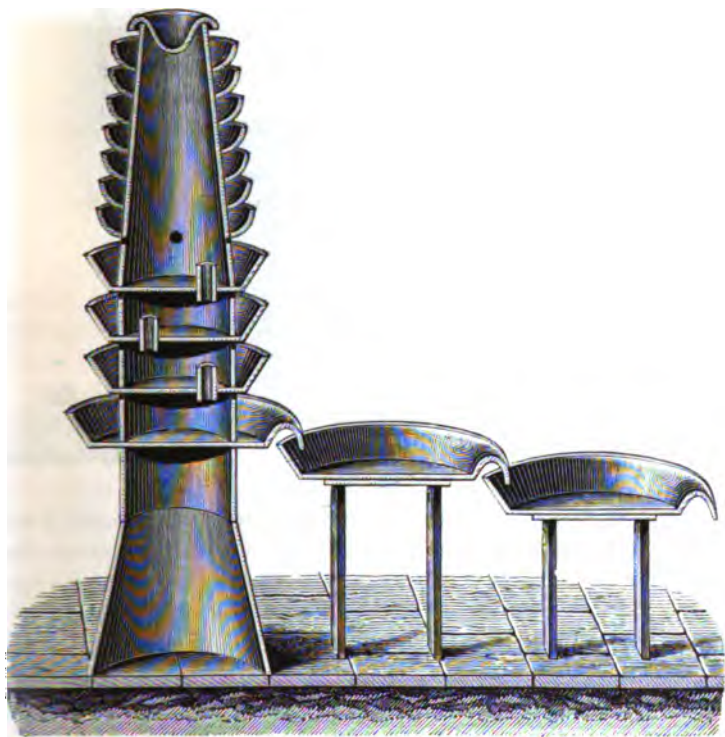


If the nitric acid were simply run into the chambers it would cause very great mischief. It would dissolve in the chamber-acid and quickly destroy the chamber-bottom; moreover, much of it would find its way outside with the chamber-acid without doing its duty within the chambers. It is therefore necessary that no nitric acid should arrive as such at the bottom of the chambers, but that, before reaching there, it should be decomposed into gaseous oxides of nitrogen. This is done by exposing it to the action of sulphurous acid, that is by the chamber-gases themselves. Before the introduction of the Glover tower, and even long after this, no other means was known for this purpose than spreading the nitric acid out over a large surface so that it was thoroughly exposed to the chamber-gases, and nothing could reach the bottom in an undecomposed state. This was done by means of stoneware or glass "cascades," of which there existed many descriptions, which are fully explained and illustrated in the first edition of this work, pp. 308 to 318. Since these cascades have been almost entirely superseded by the Glover towers, we will here show only one of the best descriptions of cascades, that made by

Fikentscher, of Zwickau, and figured in fig. 157. The acid run into its top is spread over a large surface before reaching the bottom.

A fault inherent to all such systems is this: that there is no really practical means of knowing whether the nitric acid has been entirely decomposed before the chamber-bottom is reached. The means adopted for this end at some works left much to be desired.

Fig. 157.

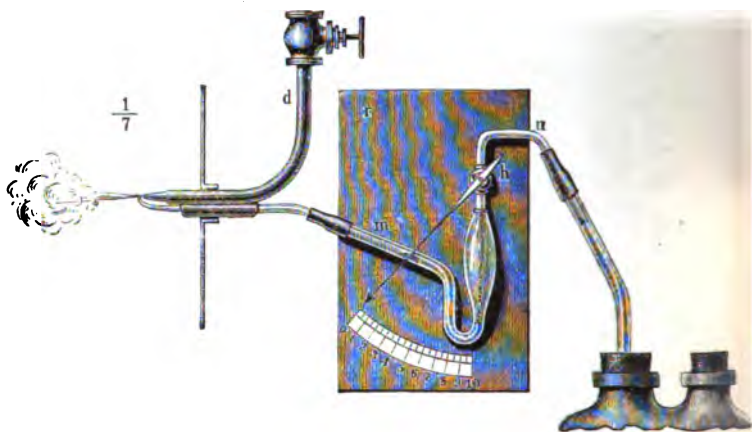


By far the simplest method of feeding, which dispenses with all cascades, tambours, &c., is that of *running the nitric acid along with the nitrous vitriol through the Glover tower*. At first few ventured to do this, because a loss of nitre was apprehended with this plan; but at most of the best-managed works it has now been done for years without involving any extra consumption of nitre, and it may be safely asserted that wherever a Glover tower in proper

working order exists, no other apparatus is required for feeding the chambers with nitric acid.

Since in exceptional cases a Glover tower is not available for the introduction of nitric acid, we shall describe a very efficient spray-apparatus, constructed for this purpose by M. Liebig (Zeitsch. des Vereins deutscher Ingenieure, 1879, p. 111). It consists of a lead steam-pipe *d* (fig. 158), with platinum nozzle,

Fig. 158.



parallel to which runs a glass pipe *m*, for conveying the nitric acid, bent up in front and drawn out into a fine point. The steam rushing past this causes a vacuum in the glass tube, and sucks acid through the latter from a stock-bottle, a glass cock *h* regulating the supply. The acid is divided into a fine mist, and none of it arrives at the bottom undecomposed.

Another apparatus for the same purpose, constructed by Mr. Stroof, of the Griesheim works, has been communicated to me by that gentleman, and is illustrated by figs. 159 and 160.

Fig. 159 shows the general disposition, fig. 160 the details of the injector *b*. The nitric acid runs from a Mariotte's bottle *A* into a Woulfe's bottle *B*, standing in a glass dish, provided with an overflow-pipe *c*, which conveys the acid, in case of the injector giving out, on to the cascade *C*. From the bottle *B* the acid is sucked away by the glass injector *b*, whose steam-jet is connected with the steam-pipe *a* by a stuffing-box. Such injectors are best

made of well-annealed water-gauge pipes, drawn out to a point. The point projects but loosely into the suction-pipe, so that a little

Fig. 159.

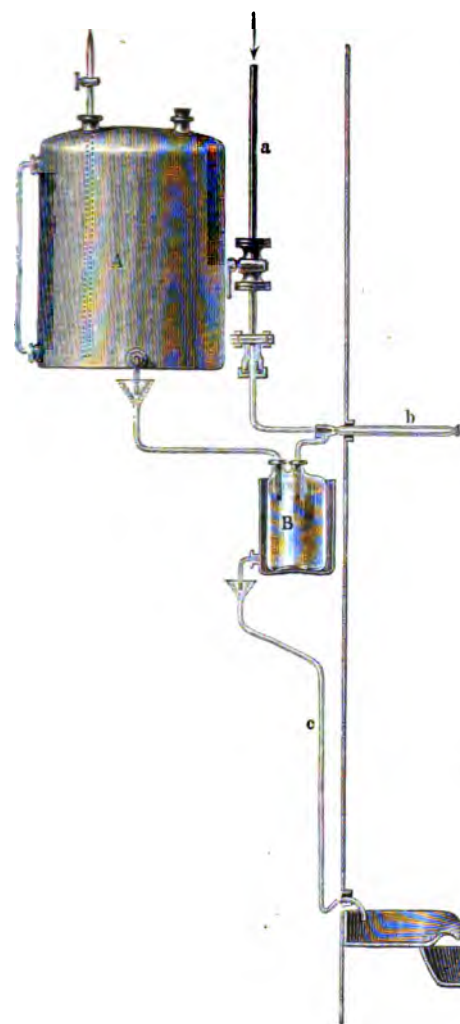


Fig. 160.



air is sucked in as well, and no breakage can take place by expansion. At a pressure of $1\frac{1}{2}$ atm. the injector can carry away 16 cwt. of nitric acid in 24 hours in the form of spray, along with a little

air. The mouth-piece of the injector must be contracted and widened out again, like that of a fire-engine, to prevent any larger drops forming at that place. The acid is thus completely converted into a mist, and a sensible saving effected in comparison with cascades.

Another glass injector for nitric acid has been described by Burgemeister (Fischer's Jahresb. 1880, p. 228).

The storing of nitric acid on the top of the chambers or of the Glover tower is generally effected in large stoneware receivers, or else in a number of smaller stoneware jars or ordinary glass carboys, all of which are connected by glass siphons, so that the running off by means of a tap-siphon need only take place from the last vessel of the set (fig. 161). Vessels proof against nitric

Fig. 161.

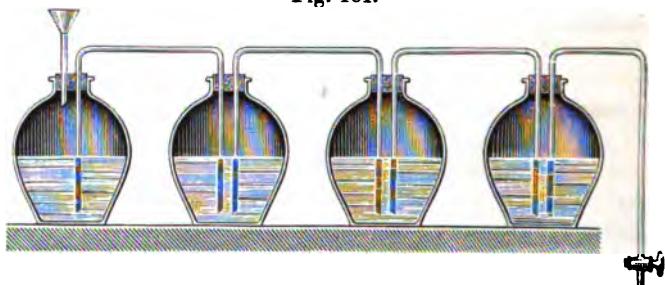


Fig. 162.



acid may also be composed of single pieces of stone joined together by a cement made of finely-ground asbestos and a dilute solution of silicate of soda, kneaded into a putty and preferably mixed with ground sulphate of baryta.

E. Pohl (G. P. 30188) employs iron vessels, lined inside with asbestos cloth soaked in paraffin. The riveting of the iron shell is effected in the manner shown in fig. 162, so that the acid nowhere comes into contact with the iron.

Introducing Nitre as an Aqueous Solution of Nitrate of Soda.

There is yet a third way of introducing the nitre. Many years ago several works ran their nitre as a *solution in water* into the chambers. This has been given up long since, both because sodium sulphate gets into the acid, which is not allowable for many purposes, and because the lead always wears away very quickly at the point where the solution enters. The same method

was patented by Burnard (14th Aug., 1875). The solution of nitre was to be injected into the chamber in a thin jet, or, best of all, at once mixed with sulphuric acid by means of a steam-jet, exactly similar to Sprengel's water-spray (compare this). The principal advantage sought for in this process was an imaginary saving of nitric acid, which in the decomposition of nitre by the burner-gas was supposed to be reduced to N_2O and N. We shall see later on that no sensible decomposition of this kind takes place at all; and any advantage accruing therefrom is far more than counterbalanced by the difficulty of keeping the nitre solution long enough in suspension to completely decompose it and to prevent liquid nitric acid from getting at the chamber-bottom. The process also takes so much steam that the acid in the first chamber gets too weak. This is certainly contradicted by the patentees (Chem. News, xxxvii. p. 203); but no independent favourable testimony has yet been published, and a saving of nitre seems out of the question. It would, however, seem feasible to run a solution of nitre through the Glover tower along with chamber-acid and nitrous vitriol, so that the nitre would be decomposed in the tower itself, sodium sulphate and nitrous vapours being formed. Of course, this plan, as well as that mentioned before, is entirely restricted to the case of all the sulphuric acid being intended for decomposing the salt. The last plan is undoubtedly the simplest imaginable one for introducing the nitre, uniting the advantages of both solid nitre and nitric acid—easy regulation, introduction of any quantity at a time, dispensing with all apparatus for introducing the nitre or manufacturing nitric acid, saving of labour and coals (in the case of nitric acid), avoiding the handling of nitric-acid carboys or of fluxed nitre cake, the latter forming an article difficult to utilize to advantage.

Unfortunately, all these advantages are counterbalanced by a great drawback, which has compelled most or all manufacturers who have tried this process to give it up: it is found that sodium sulphate crystallizes in the towers, tanks, and connecting-pipes, and causes obstructions. It would be necessary to have two Glover towers for each set, and to run the nitre solution down only one of these, whose acid would not be used for the Gay-Lussac tower, but for the decomposing-pans only. This would be very inconvenient, and for smaller works not at all feasible.

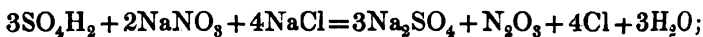
Blinkhorn (E. P. 1084, 1878) runs a solution of sodium nitrate,

of spec. grav. 1.35, in a regular jet upon sulphuric acid, contained in a pot heated by the burner-gas, and draws off the solution of sodium sulphate from time to time. This will hardly decompose all the nitrate!

Feeding the Chambers with Nitrous Gases obtained as By-products.

Several proposals partly carried out in practice have had no lasting success. Thus, for instance, the attempt has been made in France to obtain *oxalic acid* as a by-product in evolving the nitre gas by heating molasses with nitric acid and conducting the vapours into the chambers. The yield of oxalic acid, however, was not large enough to compete with its manufacture from sawdust by fusing caustic. Not more successful was a proposal of Laing and Cossins, to heat sodium nitrate with arsenious acid or chromium oxide, in order to obtain arseniates or chromates along with nitrous acid for the chamber process (Wagner's *Jahresb.* 1862, p. 207). It is also quite feasible to convey any nitrous gas generated in making arsenic, antimonie, phthalic acid, &c. by means of nitric acid, which formerly used to be lost, into the lead chambers; but this process, which (like all similar ones) can hardly be so conducted as to give a sufficiently *regular* supply of nitre to the chambers, is no longer called for, since the respective works now regularly regenerate nearly the whole of the nitric acid by mere contact of the vapours with an excess of air and water.

A peculiar process has been invented by Dunlop, and was for many years carried out at St. Rollox, but not used at the new works at Hebburn belonging to the same firm. A mixture of common salt, nitrate of soda, and sulphuric acid is heated in large iron cylinders; the principal reaction setting in is as follows:—



but the further deoxidation of nitric acid will only be prevented by keeping within certain limits of temperature. Thus there remains a soluble residue of sodium sulphate, whilst chlorine and nitrous acid are given off in a gaseous form. The two gases are separated by passing them through a series of leaden Woulfe's bottles filled with sulphuric acid of 1.75 spec. grav. which retains the nitre-gas, being converted into "nitrous vitriol" and used as such (see below); the chlorine passes through without absorption,

and is utilized for bleaching-powder. The advantage of this process is, that chlorine is obtained direct from salt without making any muriatic acid and without wasting manganese. The drawbacks are :—that the nitre-gas has to be evolved again from the nitrous vitriol, which formerly could only be done by diluting with hot water, necessitating a reconcentration of the vitriol; that there is a danger of losing nitrogen compounds; and that the apparatus is somewhat complicated.

At the Uetikon works, near Zurich, nearly all the water required for the chambers is obtained in the manufacture of iron mordant for dyeing purposes. This is made by treating copperas with nitric acid, and thus oxidizing the ferrous to ferric sulphate. The nitric acid is thereby reduced mostly to nitric oxide, partly also nitrous acid; these gases are conveyed into the vitriol-chambers, and there do exactly the same duty as if the nitric acid had been directly supplied to the chambers. Recently the manufacture of cupric sulphate from metallic copper, sulphuric and nitric acid has been introduced at the same works, equally carrying all the nitrous vapours into the vitriol-chambers.

The Steam

is always generated in an ordinary steam-boiler since boilers placed above the burners have been given up everywhere. The boilers are constructed in the usual manner, but are mostly made for low pressure, rarely working above two atmospheres, more frequently only at one or one and a half atmosphere; in the south of France they work at three or three and a half atmospheres. A high pressure has no object so long as the liquid is spread over the whole chamber-space; for even low pressure fulfils this requirement and sufficiently assists the draught. Low-pressure steam is more easily kept at the same tension than high-pressure; without this no regulation of the supply of steam to the chambers by the attendant is of any avail. High-pressure certainly condenses less readily than low-pressure steam; but this is a doubtful advantage, so long as the steam possesses enough "carrying-power" to convey the minute globules of water right to the other end of the chamber. Experience has shown that this is the case even with low-pressure steam; at most English works they only employ a single jet at one end of each chamber, and find this quite sufficient to supply the whole chamber with moisture.

Of course low-pressure steam may be obtained from a boiler working at high pressure, by means of a reducing-valve, and thus at small works the same boiler may be made to do duty for supplying the chambers and for driving the machinery of stone-breakers, air-pumps, and so forth.

It is also almost a matter of course that the chambers may be fed with the exhaust-steam of engines, if these are worked in such a way as to leave some pressure in the exhaust. The utilization of the waste steam of the Gay-Lussac air-pump for this purpose had been practised by myself for many years, as described in the first edition of this work, vol. i. pp. 393 & 565. A proposal not essentially differing from this has been patented by Sprengel, No. 10798, 1886.

At some large works, in order to control the regularity of tension of the steam, so important for a regular chamber process, *registering steam-gauges* are employed, which show the tension during the whole day on a sheet of paper wrapped round a drum making one revolution in twenty-four hours. Such a gauge, made by Schaeffer and Budenberg, of Magdeburg, is described in 'Dingler's Journal,' ccxxvii. p. 519.

The *conveyance of the steam* to the chambers usually takes place in cast-iron pipes, with one or more branches for each chamber. The main pipes in any case, and, if possible, also the branch-pipes, looking at their great length, ought to be surrounded by bad conductors of heat to restrict radiation as much as possible, and avoid a considerable loss by condensation of water.

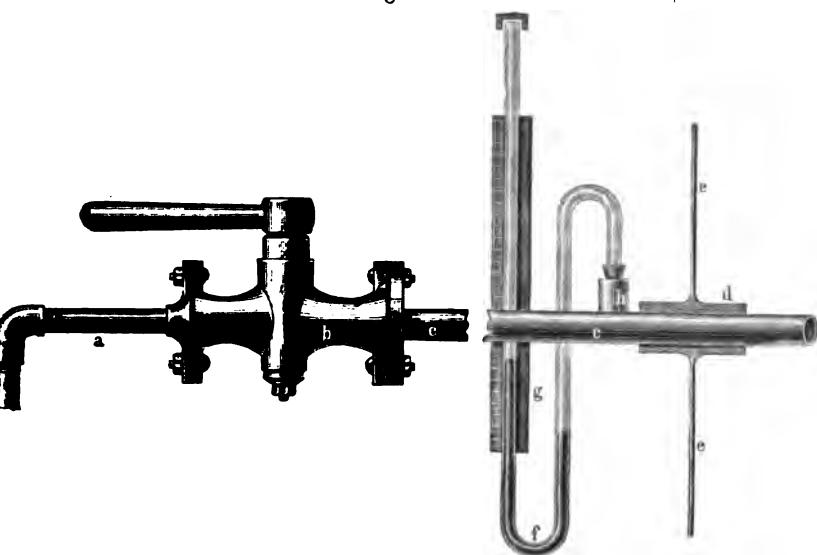
The pipes must always be laid with a slight fall towards the boiler, so that the condensed water may run back. Where, from local circumstances, this cannot be done, automatic apparatus for removing the water should be fixed at the lowest points.

Of course the size of the main pipes must correspond to the number and size of the chambers. When more than one steam-boiler is required, they are placed together, and their main pipes connected so as to equalize the pressure. The *branches* for each chamber need not be above 1 inch wide, even for large chambers (up to 70,000 cubic feet) supplied by one jet. They are made of wrought-iron tubes, *a* (fig. 163), sometimes of copper, up to a short distance from the chamber, where they end in a cock or valve, *b*, to which a lead pipe, *c*, equal in width to *a*, is attached and projects into the chamber itself. It is not, however, burnt to the

chamber-side *e* itself; but a short wider tube, *d*, is burnt to this, and *c* is loosely put into it, the joint being made tight with tar, cement, &c. Sometimes in lieu of this an india-rubber cork is employed, but this does not last long. In this case, if the outlet is stopped up by lead sulphate, the pipe *c* can be easily drawn out and cleaned, and no platinum nozzles are required (as had been proposed by Scheurer-Kestner).

The same figure shows another commendable contrivance, viz. a simple mercurial *pressure-gauge*, consisting of a bent glass tube, *f*, with a scale, *g*, put by means of a caoutchouc bung into a branch, *h*, of the lead pipe *c*. Thus the pressure *behind* the regulating cock

Fig. 163.



can be observed at any time; and the chamber-manager has thus a means of very exactly regulating the supply of steam. Any water condensed in the gauge can be easily allowed for.

A good steam-cock is preferable to a wheel-valve, because the wheel does not show how far the valve is opened, whilst the handle of the cock can be fitted with a graduated arc so that its position can be fixed with precision.

Automatic steam regulators, if reliable, save a great deal of trouble, but do not dispense from constant supervision on the part of the attendant, as they are somewhat liable to get out of order.

In England the usual way is this: to employ only one jet of steam for each chamber, mostly beside, above, below, or even within the pipe conveying the gas from the burners, the Glover tower, or the preceding chamber. Some introduce the steam quite near the top, others in the centre of the chamber-end. A single steam-jet suffices, if the length of the chamber does not exceed about 130 feet; in longer chambers it would not carry right through.

Experience has shown that a single steam-jet from a 1-inch pipe is quite sufficient for feeding chambers up to 130 feet length, and also that the distribution of moisture through the chamber is properly effected. By arranging a single steam-jet, the cost of cocks, branches, &c. is saved, and the regulation of the supply of steam is much simpler and easier than if, for instance, four cocks were to be opened one quarter as much as the cock of the single jet. It is also true that in this way the first part of the chamber, which makes most acid and evidently requires the greatest supply of moisture, actually receives it, and in practice the English system works well up to the length of chambers indicated.

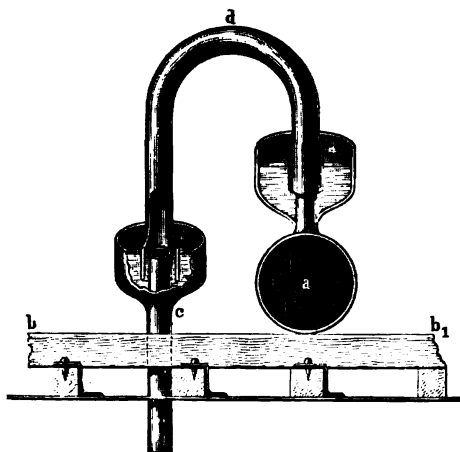
On the Continent most manufacturers prefer to employ a number of steam-jets for each chamber, so as to make themselves independent of any casualties in the proper distribution of steam by a single jet. These branch jets are introduced at right angles to the direction of the gaseous current either in the long chamber-sides, not far from the top, or, which is the most usual case, through the roof of the chamber, so that the single jets can be regulated when walking over the top. Thus, for instance, at the Oker Works there is a steam-pipe extending above the chambers, from which, at intervals of 17 feet, branches of $\frac{3}{4}$ -inch bore enter the latter; from these the steam issues, by several small openings immediately below the top, in several directions. The tension there is 2 atmospheres (Bräuning, Preuss. Zeitsch. 1877, p. 137). A similar arrangement exists at Aussig and elsewhere. In all these cases each branch-cock must be regulated separately.

Where there is a Glover tower, the first steam-jet need not be in front of the first or "leading" chamber, as this part receives enough steam from the Glover tower; the first steam-jet may be 20 or 30 feet further on.

An apparatus by which steam can be introduced at many places and yet regulated at a single place has been described by Scheurer-

Kestner (Wurtz, Dict. de Chimie, iii. p. 149); it is shown in fig. 164: *a* is the copper main pipe running in the centre of the chamber-top, and held fast by the joist *b b*₁, as well as the branches *c*. The latter are arranged alternately on the left and right hand at distances of $16\frac{1}{2}$ feet; they are made of lead, pass through the chamber-top, and are burnt into it. The arm *d*, covered with straw rope, serves for making the communication between *a* and *c*. Both pipes have hydraulic lutes, so that only a very low pressure can be employed. The main pipe, *a*, is provided with a cock, and the supply of steam regulated by this. The

Fig. 164.



steam, entering the pipe at the front end of the chamber, will principally escape through the first branches, where it is most needed, because in the beginning most unchanged sulphurous acid is present. The pipe *a* has sufficient fall for emptying the condensed water. (This arrangement seems to offer no advantage over simple branches on a main pipe, and has the great disadvantage that only a very low pressure can be employed, as the water is easily thrown out of the hydraulic joints of *a* and *c*.)

Perfectly absurd is the arrangement given in every edition of Payen's 'Précis,' even up to the last one (1877), and copied from it into many other treatises. Here the steam-jets are shown partly in the chamber-bottom, coming through the chamber-acid. No practical man can imagine that this plan, if it has been actually

carried out anywhere, has not been abolished at the first opportunity; for the shaking by the steam must gradually cause a leakage at the joint, which cannot be got at, owing to the chamber-floor; nor can it be repaired till the chamber has been entirely emptied.

The total quantity of steam required for a set of chambers, which should be known approximately in order to fix upon the boiler-space and the size of the main pipes, of course depends, first, upon the quantity of sulphur to be burnt, secondly upon the existence of a Glover tower, and thirdly upon the strength to which the acid is brought in the chambers. A general rule, therefore, cannot be laid down. The two latter conditions are partly reciprocal; the stronger the acid is made in the chambers, the less water is evaporated in the Glover tower, and *vice versa*. If we assume, adopting a very usual proportion, that all the chamber-acid is brought up to 124° Tw., and that it is concentrated in the Glover tower up to 148° Tw., the amount of steam required will be as follows:—

Each pound of sulphur burnt requires,

$$\text{1st, for forming } \frac{98}{32} \text{ SO}_4\text{H}_2, \frac{18}{32} \text{ water} \dots\dots = 0.5625 \text{ lb.}$$

2nd, for diluting it down to 124° Tw.

$$(\text{=70 per cent. SO}_4\text{H}_2), \frac{30 \times 98}{70 \times 32} \dots\dots = 1.3125 \text{ ,,}$$

$$1.8750 \text{ ,,}$$

Of this nothing is lost with the escaping gas, as this passes in the Gay-Lussac tower through strong vitriol; on the contrary, the Glover tower saves the steam corresponding to a concentration from

124° (=70 per cent.) to 148° Tw. (=80 per

$$\text{cent.}), \text{ viz. } \frac{10 \times 98}{70 \times 32} \dots\dots = 0.4375 \text{ lb.}$$

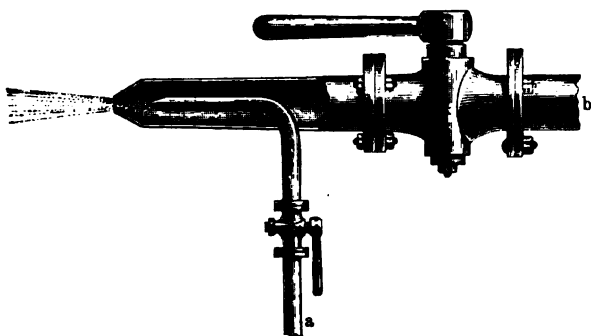
$$\text{Leaving} \dots\dots\dots 1.4375 \text{ lb.}$$

which must be supplied to the chambers. To this must be added a certain quantity for water condensing in the steam-pipes; but

this cannot be estimated generally, since here everything depends upon the length of the pipes, their thickness, surroundings, &c. It is safe to say that the steam to be generated in the boiler, without a Glover tower, amounts to about $2\frac{1}{2}$ —with it, to about 2 times the weight of sulphur burnt.

In lieu of feeding the chambers with steam, Sprengel (patent of October 1st, 1873) proposed liquid water in the form of a

Fig. 165.



fine spray. His reasons are these:—that the steam increases the volume of the gases by its heat, and consequently more chamber-space and nitre are used, which can be avoided by introducing the water in a liquid form, sufficiently divided; and that the cost of evaporation can be saved in this way. The water is itself made into a spray by the employment of steam, since a steam-jet of 30 lb. tension escapes through a platinum nozzle in the centre of a water-jet, as shown in fig. 165 (where *a* is the steam-pipe, *b* the water-pipe); but 20 lb. of steam is sufficient for converting 80 lb. of water into a mist. Such jets are arranged in the chamber-sides, at distances of 40 feet from each other, and supplied with water from a tank fixed at some height above. Sprengel assumes that two thirds of the coals can be saved in this way, instancing the works at Barking Creek, where at the same time a saving of $6\frac{1}{2}$ per cent. pyrites and of $14\frac{3}{4}$ per cent. nitre is said to have been effected. At those works there was no Gay-Lussac or Glover tower. In the case of factories working with a Glover tower, Sprengel estimates the saving in coal at a third less (Chem. News, xxxii. p. 150). Of course the water- and steam-cocks must be exactly regulated, and the two nozzles must have a particular

shape, so that only a fine mist and no coarser drops shall be formed, which would at once fall to the bottom and only dilute the chamber-acid.

A different way of producing a spray or mist of water instead of a steam-jet for feeding vitriol-chambers is employed at the Griesheim works, and has thence been introduced with great success into other works. The spray is here not produced by an injection of steam, but by allowing the water, at a pressure of two atmospheres, to issue from a small platinum jet against a platinum button. Two rows of such water-jets are introduced through tubes in the chamber-top, each tube about 20 feet apart from the other. Thus the whole chamber is uniformly filled with a fine mist, which together with the steam coming from the Glover tower, supplies all the water required for the chamber-process. The water must be carefully filtered, as otherwise the jets would soon be stopped up; but this trouble is far more than compensated by the considerable saving in fuel, caused by doing away with the chamber boilers. The fear formerly entertained, that the introduction of the moisture in the shape of liquid water would reduce the temperature of the chambers below that most favourable for the acid-making process, is entirely groundless. At Griesheim it was observed that the temperature of the gases, arriving from the Glover tower sometimes at only 35° C., quickly rose within the chambers to 50° C. Similar observations have been frequently made; most extensively by Lunge and Naef (Chem. Ind. 1884, p. 17). This is explained by the fact that the evolution of heat, consequent upon the chemical reactions going on within the chamber, is far more important than the heat brought in by the steam, and that, in fact, the local cooling produced by the water being supplied in the liquid form is actually beneficial in most cases (comp. next Chapter).

It might be objected to the introduction of the water in the shape of a spray, that steam is preferable on account of being only gradually condensed in its onward course within the chamber, and that the moisture would thus be more uniformly distributed through the chamber. But this objection is not at all valid, and would not be so even if no sulphuric acid were present in the chamber. Calculation shows that the gas introduced for each kilogram of sulphur, whose volume at 50° C. and 760 millim. pressure amounts to 8345 litres, can contain only 0.6868 kilogram

of aqueous vapour, whilst the total amount of water is nearly four times as much, and three fourths of the steam entering into the chamber must therefore be at once condensed into water. This calculation, given in our 1st edition, pp. 348 & 349, is not repeated here, since it does not take into account the fact that the tension of aqueous vapour within the chamber is very much reduced by the presence of sulphuric acid, and it is hence useless for our purpose. Dr. Hurter (*J. Soc. Chem. Ind.* 1882, p. 51) somewhat more correctly applies to our case Regnault's table for the tension of aqueous vapour in sulphuric acid of various strengths, and he there gives a diagram which allows of finding this tension for any intermediate concentration of acid. But this is also incorrect for the principal working part of the vitriol-chamber; for Regnault's determinations only go as far as 35° C., that is far below the ordinary chamber-temperature, and it is not admissible to calculate tensions at 60° , 80° , or even higher temperatures by simply applying Regnault's table or Hurter's diagram to them. This gap has been filled by a set of elaborate observations made by Sorel, and first made accessible to the public by me (*Zeitsch. f. angew. Ch.* 1889, p. 272). Sorel's table extends to acids from 44 to 82 per cent. H_2SO_4 , and to temperatures from 10° to 95° . We have given it in the third Chapter, p. 137, where the specific gravities corresponding to the acid percentages have been added for the reader's convenience. At the close of this chapter we shall give a table for reducing volumes of gases to the conditions of the vitriol-chamber atmosphere, which equally takes into account the aqueous-vapour tensions of sulphuric acids of various strengths.

The importance of this table will be indicated at present only by one example. In a special instance the temperature close to the chamber-side was 80° ; the acid running down the side stood at 114° Tw. = 66 per cent. H_2SO_4 , and the aqueous-vapour tension at this place was, therefore, = 39 millim. Only 6 centim. (say $2\frac{1}{2}$ inches) within the chamber the temperature was already 95° ; but at this temperature an acid, whose aqueous-vapour tension is = 39 millim., must have a strength of $128\frac{1}{2}^{\circ}$ Tw. = 72.33 per cent. H_2SO_4 , and this was found to be really the case. We shall see the importance of this in Chapter IX.

Looking at the great reduction of the tension of aqueous vapour by the presence of sulphuric acid, we must conclude that the

steam introduced into the chamber must be condensed almost immediately into a liquid mist, and this must reduce the alleged superiority of steam in "carrying power" to a properly comminuted spray of water, introduced at high pressure, to almost *nil*.

Of course the water *must* be properly comminuted; otherwise, that is when it drops from the jets in the shape of rain, it dilutes the chamber-acid to an intolerable degree, and this is all the more injurious as this dilute acid floats on the top of the stronger chamber-acid, and is not noticed for a long time at the places where the acid is drawn off, till it becomes too late to meet the evil at once. This accident will happen whenever the jets are out of order, and this has caused several works to abandon the plan of introducing the water in the shape of a liquid spray.

A very good shape of platinum jet, for converting water or acid liquids into a thin spray, has been constructed by F. Benker, of Paris, and is shown in fig. 166. In this jet the distance between the nozzle *a* and the disc *b* is adjustable, the disc being moved backwards or forwards by means of a rod, on the top of which is cut a fine thread, which works in a similar nut *c*, placed on the top of the cylinder. The screw and nut are made of an alloy of platinum and iridium, so that there is no fear of their wearing out. In this manner the best distance between *a* and *b* can be easily attained, and by removing *b* altogether the nozzle *a* is easily cleaned.

Körting Brothers' spray producer (fig. 167) (Zeitsch. f. angew. Chem. 1888, p. 404) contains within the contracted part a metal spiral, which by the pressure of the liquid is kept tightly in its place, whilst the liquid on passing through the helicoidal channel takes a rotating movement, so that, on issuing, it is projected equally on all sides as a conical spray. The nozzle and spiral spring

Fig. 166.



Fig. 167.



can be arranged for spray of any degree of fineness. This apparatus was originally intended for damping the air in cotton-mills &c. for precipitating dust, for absorbing acid vapours, and so forth. It has also been made of platinum, and is in several places used for producing a fine spray of water in vitriol-chambers.

*Arrangements for producing the Draught in the
Acid-chambers.*

Already, when treating of the burner-gas, we have had to notice the draught which is necessary in the whole set in order to keep the process of combustion and acid-formation going; and we have seen that the hot gaseous mixture in itself contains the conditions for causing a draught, since it is much lighter than the air, and thus will always have a tendency to rise from the burners to the chambers. We have also pointed to another potent source of draught, viz. the formation of liquid sulphuric acid within the chambers from the mixture of the gases, which must necessarily have an aspirating action, although not only from the burners, but from all sides.

Along with these two sources of draught furnished by the essence of the acid-making process itself, there must always be another arrangement for causing further draught, especially because otherwise the current of gas could not be turned into the required direction. In the simplest case a plain *outlet-pipe* behind or above the last chamber will suffice. The Belgian Commission of 1854 even preferred this arrangement to a chimney, because this might produce an excessive draught; and many factories work quite well in this way. But it cannot be said that the excessive draught of a chimney leads to a loss of uncondensed gas and too quick a passage through the chambers; for it is always very easy to cut off an *excess* of draught by a damper &c. in the outlet; but it is nothing like so easy to increase the draught if *insufficient*. For the latter object a *steam-injector* is the most convenient apparatus. Sometimes, in lieu of a proper injector, a simple steam-jet, turned in the direction of the draught, is employed; but this is a very wasteful proceeding, and a proper Körting's injector, made of regulus metal (lead and antimony) should be always employed. Such injectors can be applied in various places. Scheurer-Kestner (Bull. Soc. Chem. xlv. p. 98) describes his experience in that

way. He employed a Körting's injector which produced a gaseous mixture of 7·9 per cent. steam and 92·1 per cent. air. Thus a quantity of 1814 kilog. of water in the shape of steam sufficed for aspirating the air required for burning 7000 kilog. of 45 per cent. pyrites. At first the injector was placed in the pipe entering into the first chamber. This is the best place, where there is no Glover tower, as the steam is in this case very serviceable for working the chambers, and thus costs nothing; but in case of a Glover tower this produces an excess of steam in the first chamber. The regulus metal of the injector wore out pretty quickly; nor could it be replaced by porcelain, which cracked very soon; a thin casing of platinum, however, was found efficient for protecting a regulus injector. It was tried to place the injector between the first and second chambers, but here also too much steam was introduced into the chamber. This is avoided by applying the injector at the exit from the Gay-Lussac tower; but then all the steam is lost, and the process is thus made expensive. In the case of seleniferous pyrites the injector between the burners and the chambers is stopped up so quickly with a deposit of selenium, that two injectors must be employed side by side, one of which can be cleaned out while the other one is going.

At the works of Messrs. Matthiesen and Hegcler at La Salle (Ill.), where zinc-blende is roasted in a mechanical shelf-burner and the necessary draught for the chambers could not be obtained by a chimney, an iron fan-blast, covered with an alloy of lead and antimony, is placed between the Glover tower and the first chamber, and another such apparatus between the Gay-Lussac tower and the chimney. This arrangement had been working for several years when I visited the works in 1890.

It must not be overlooked that with steam-injectors a regulation is all the more called for, lest the draught should be too strong; and in the end a cheap source of draught, viz. the chimney, has been replaced by a dear one, without any gain as to constant supervision and regulation. We should accordingly always prefer a chimney to a steam-jet, all the more as the former will always be necessary in any case for the steam-boilers. Of course the chimney, to do its work, must be higher than the chambers.

It comes to the same thing as a chimney if the outlet-pipe fixed to the last chamber has a considerable height—for instance, 50 feet (in the south of France). Where several sets of chambers exist in the same works, it is preferable to carry them all into a common

chimney, providing the connecting-pipe of each set with a contrivance for regulating the draught. It is not a good plan to utilize for the chambers a chimney with which ordinary furnaces are connected, as the draught will be of a very variable character in this case, and the working of the chambers will not be easily kept entirely regular. Still, at some works this plan cannot be avoided, and must be provided for by more careful regulation of the draught. In such works more than anywhere else the automatically acting dampers, described below, are recommended to be used.

The employment of a chimney is even more advisable if, as is now the case in all well-appointed works, a Gay-Lussac tower is fixed at the end of the set. In this case the draught must be regulated with even greater care than otherwise; but there must be an excess of draught at disposal to begin with. It is also a great convenience if the "sight" necessary for checking the work of the tower (comp. Chap. VIII.) can be arranged in the down-draught near the ground-level, or at least the gangway round the chambers. If there is no down-draught, but a direct top-draught out of the tower, it is always necessary to mount to the top to observe the "sight." It is certainly quite possible to employ the tower itself as a chimney, if it is built with its top a good deal higher than the chambers; and this is actually done at several works, but probably in some cases only because there is no chimney available. The drawbacks of this plan are well illustrated by the following passage from the official Alkali Reports, No. 21 (for 1884), p. 74:—"No. 2256. The vitriol-exit from the plant in which the pyrites smalls are burnt used to be at the top of the Gay-Lussac tower. I found an exceedingly high escape from here on my first three visits. The manager has since connected this exit to the main chimney, and now finds he can better regulate the draught on his chambers. Since this has been done the tests have been invariably good."

The more recent sets of chambers at Oker, utilizing the configuration of the ground, are arranged in such a way that the burners, Glover towers, chambers, and Gay-Lussac towers rise one above the other, terrace-wise. The outlet of the whole is at a height of 62 feet above the level of the burner-grates. Drawings of this arrangement are given by Bränning (*Preuss. Zeitschr. f. Berg-, Hütten- u. Salinenwesen*, 1877, table ii.). It is stated there that formerly the draught could not be made sufficient, even by connecting the Gay-Lussac towers with the boiler-chimneys; but this

only proves that the latter had not the necessary excess of drawing-power. With this expensive plan, followed at Oker, there is the convenience connected of running both the chamber-acid and the Gay-Lussac acid into the Glover tower by natural fall; but the latter could only be made 17 feet high.

It has been noticed at Oker that a very long draught-pipe, connecting the last chamber with the tower, affords the advantage of neutralizing to some extent the oscillations of the outer atmospheric pressure, and thus facilitating the regulation. Be this as it may, such a long pipe, although it causes some loss of draught by friction, will always be very useful, by cooling the gas previously to entering the absorbing-tower.

C. L. Vogt has patented (on July 29th, 1875) a peculiar contrivance for producing draught in acid-chambers, which introduces the air along with the necessary steam through a pipe with an opening of $\frac{1}{4}$ inch. The steam is under a pressure of 3 to 4 atmospheres. Such a contrivance is only exceptionally called for; but there are cases in which a supply of air behind the burners seems desirable (7th Chapter).

At some factories they work in this way: the Glover tower is packed very loosely, and itself acts as a chimney, so that the burners have always very good draught and never blow out, whilst it is quite possible at the same time to keep the exit draught so low that there is some little outward pressure even in the last chamber. In the next Chapter we shall describe an arrangement by which this aim can be attained even more perfectly.

We have already said something about the principles according to which the supply of air must be regulated; and we shall have to come back to this in the next Chapter. Here we must only remark that there must be in any case enough total draught *behind* the chambers, but not too much; otherwise, even if the burners themselves are protected against excess of draught by diminishing the air-holes below the grates, there is all the more tendency for air to enter the chambers from all other sides through the finest chinks and thus disturb the process. If the draught is excessive, the incubus of the vitriol-maker, pale chambers, at once makes its appearance.

Whether, therefore, the draught is produced by a chimney or by an open pipe, there must always be some contrivance *for regulating* it. At many works this is done by a simple damper, introduced into the respective lead pipe by a slit, luted with clay or not at all.

Fig. 168.



Fig. 169.



The arrangement shown in fig. 168, partly in elevation, partly in section, and in fig. 169, in cross section, is far more perfect. The draught-pipe, *a a*, is widened out into a rectangular vessel surrounded by a jacket, *b b*, forming an hydraulic joint; and the damper, *c*, is surrounded on all sides by the jacket *d d*, dipping into the water lute at *b*. The damper is raised and lowered by the help of the chain, pulley, and balance-weight, *e, f, g*.

In continental works the arrangement shown in fig. 170 is frequently met with. The draught-pipe, *a a*, is interrupted by a

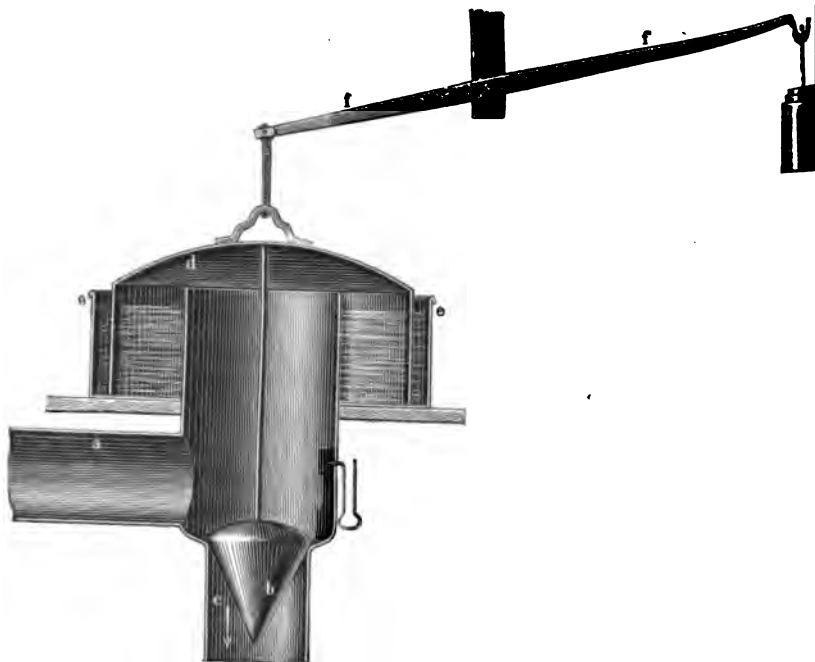
Fig. 170.



wider drum, *b*, divided into two parts by a horizontal diaphragm, *c*. The latter is perforated by a number of holes whose total area is somewhat larger than that of the pipe, *a a*. When, therefore, all the holes are open, there is no obstacle whatever for the draught; but this can be produced at will by closing a certain number of the holes with clay or lead plugs. For this purpose the space above the diaphragm is accessible by a small door, which may consist of a pane of glass, *d* (fig. 170), to which another on the other side corresponds, so that the whole at the same time serves as a "sight."

Automatic regulation of the draught in the chambers.—Especially in the case of chambers not connected with a high chimney, where changes of wind &c. produce great variations of draught, it is advisable to adopt some automatic regulation along with the ordinary dampers, &c. Such an automatic apparatus can be made by putting on to the horizontal part of the exit-pipe a perpendicular 12-inch pipe, closed by a bell standing in an annular water lute.

Fig. 171.



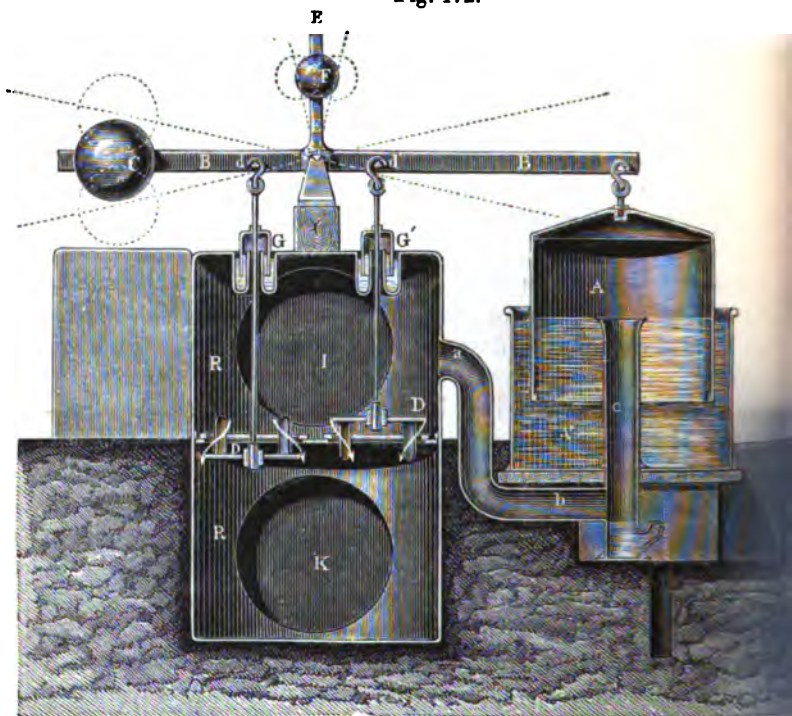
The bell hangs on one arm of a lever, whose other arm is so weighted that the bell can travel freely. When the draught is just right, this second arm has a certain position, in which a throttle-valve within the exit-pipe connected with it is half open. When the draught increases, the bell descends, owing to the increase of atmospheric pressure, and partly shuts the throttle-valve; in the opposite case of the draught decreasing, the throttle-valve is opened wider. This apparatus, as constructed by M. Delplace, and employed by him for the last ten years with the greatest advantage, is shown in fig. 171, where *a* is the entrance-pipe from the Gay-Lussac tower, *c* the exit-pipe, *b* a conical valve, *d* the regulating bell, *e e* the water-line of the hydraulic joint, *f* the lever, *g* the balance-weight.

Somewhat different in detail, and apparently very accurately working, is the apparatus of Mr. W. G. Strype, of Wicklow, of which the following is a description (patent No. 705, Feb. 21st, 1879):—

The accompanying drawings illustrate two forms of the apparatus, fig. 172 being the most desirable, although somewhat more expensive in construction than the arrangement shown in fig. 173. Referring to fig. 172, an inverted vessel or receiver *A*, open at its lower end, dips into a tank *A*¹, containing water or other suitable liquid acting as a hydraulic joint. The interior of *A* is placed in communication, by means of the pipe or passage *a b c*, with a receptacle *R* connected with the main flue from the absorbing-towers and chambers. This receptacle is also in communication with a flue leading to the chimney, or other device for supporting the draught, and is divided by a partition having apertures fitted with valves or dampers *D D*, made of an alloy of lead and antimony. The operation of opening and closing *D D* to ensure uniformity of draught is regulated automatically by the action of the suction itself in the following manner:—The dampers are connected to a lever *B*, mounted and turning on a centre or fulcrum *e*. Suspended from one end of the lever is the vessel *A*, whilst the opposite end is loaded with a weight *C*, sufficient to preponderate to the required extent over the load of *A*. Assuming that the draught has an excess of “pull” over that which is adjusted and necessary for the proper working of the chambers, the dampers being open, the suction within the vessel *A*, when accelerated, will draw down that end of the lever and elevate the opposite or

weighted end, and so partially close the dampers. C is so calculated that the weighted end of the lever can only be elevated when the

Fig. 172.



required draught is exceeded, and it will fall by gravitation as soon as the draught is unduly diminished. It follows that thus the desired uniform action is obtained.

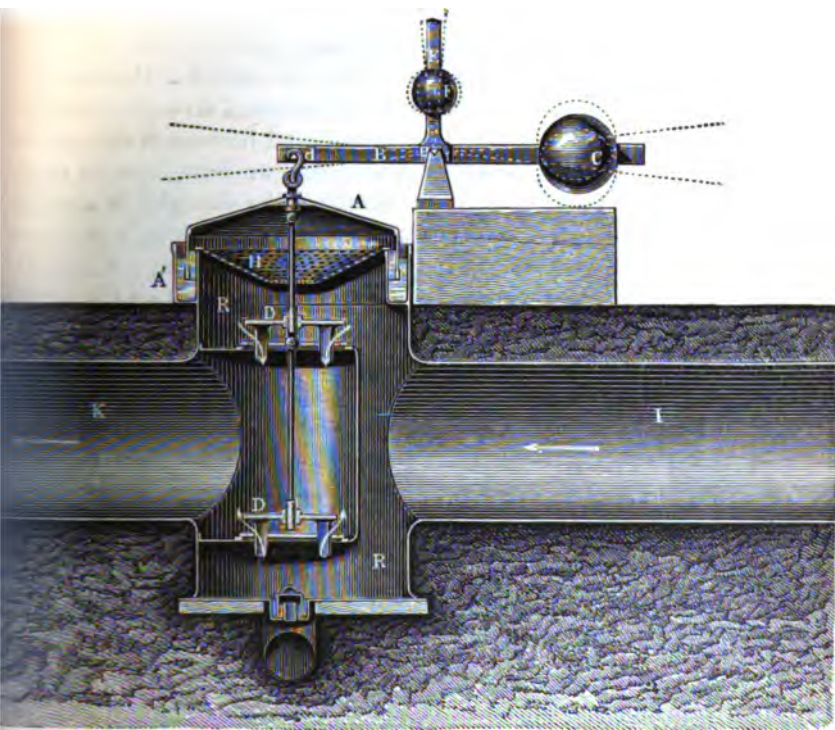
The connection between the dampers and the lever B is by means of rods or links passing through water-sealed stuffing-boxes, G G'; and to avoid friction these rods are suspended from knife-edge centres $d d'$. The other centres are constructed with knife-edges in like manner.

The vessel A becomes sensibly *lighter* when deeply immersed in the liquid, owing to the thickness of the sides, and would thereby constitute a source of disturbance to the proper action of the apparatus. To counteract this, the lever B is provided with a projecting

arm E, carrying an adjustable weight F, arranged in such a position that, as the arm partakes of the motion of the lever, the centre of gravity of the system will be moved in the direction and to the extent necessary to effect the required correction.

Fig. 173 is a simpler, and in some applications a more convenient

Fig. 173.



form of the apparatus, the action being of course identical with that described for the arrangement in fig. 172. Should the draught fluctuate very much, the diaphragm shown dotted at H (with an opening in its centre to communicate with the vessel A) can be interposed to prevent the movements of the regulator being too sudden and rapid.

This apparatus has no wearing surfaces, is practically frictionless in its working, and is balanced in all positions. By means of it

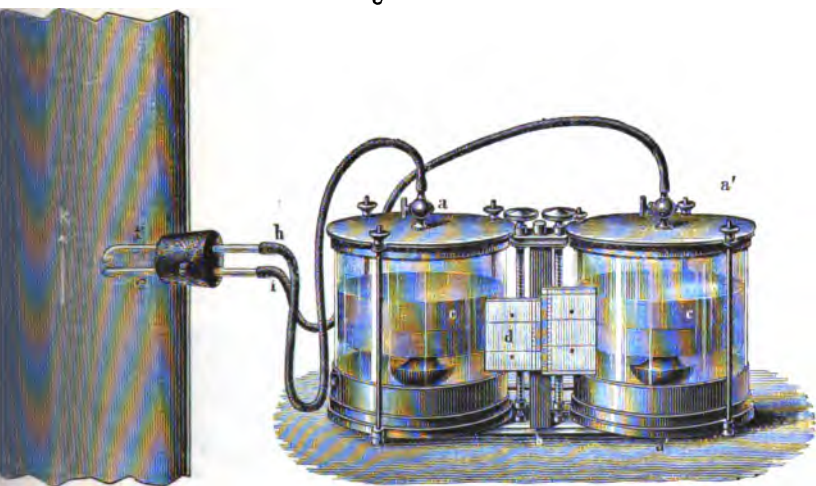
any disturbance to the steady and uniform flow of gases through the chambers caused by irregular chimney-draught is prevented, the admission of air to the burners is more uniform, the regulation of the proper quantity and relation of the gases to each other throughout the chambers is facilitated, and better working and more economical results are obtained in the process with less supervision and attention than hitherto required to carry on successfully the manufacture of sulphuric acid.

Anemometers.

Although we have in a previous Chapter excluded the use of a Combes' anemometer for regulating the access of air to the burners, because it is too delicate an instrument, and because it only shows the draught in the place which it occupies, we have here to speak of an anemometer adapted for controlling the draught in another place, viz. on leaving the chambers. This is Péclet's *differential anemometer*, as modified by Fletcher and Swan. Fletcher's modification is described in the Third Annual Report on the Alkali Act, 1863, by the Inspector, for 1866, p. 54 *et seq.*; Swan's in the 'Transactions of the Newcastle Chemical Society,' Jan. 26, 1871. Since this instrument can also be employed usefully for other purposes (as for the muriatic-acid condensers, the sulphur-recovery by Mond's process, and the chimney-draught generally), we shall here give a description of it. It is founded upon the physical principle that a current of air passing the open end of a tube causes a partial vacuum in the tube. If, therefore, a straight tube is introduced through a hole into a chimney, or into the draught-pipe, taking away the chamber-gas, so that the gaseous current passes the open end of the tube at a right angle, a partial vacuum will be formed in the latter, proportionally to the velocity of the current. But the aspirating action of the chimney will be equally communicated to this tube; and we must here distinguish between these two actions. To do this, we must introduce two tubes into the chimney, one of which ends straight, whilst the other one is bent to a right angle, so that the current of air blows into it. Both tubes will now be affected by the aspirating action of the chimney; but in the straight tube this is *increased* by the aspirating action of the current crossing its open end, whilst in the bent tube it is diminished by the air blowing into it. The difference between the aspirating action of the two tubes is thus reducible to the action of the current

of air; and by measuring it the speed of that current can be ascertained. For this purpose the two tubes are connected with a U-shaped glass tube containing water or another liquid; this will rise in one of the limbs to an extent corresponding to the difference of suction. Since the sucking-action of the chimney acts upon both limbs, it is eliminated, and the difference of level corresponds merely to the different action exerted by the current of air upon the straight tube, which it crosses, and the bent one, into which it blows. This action rises and falls with the speed of the current; and the latter accordingly can be deduced from it. Water (used by Péclet), on account of the friction exercised in the U-tube, is

Fig. 174.

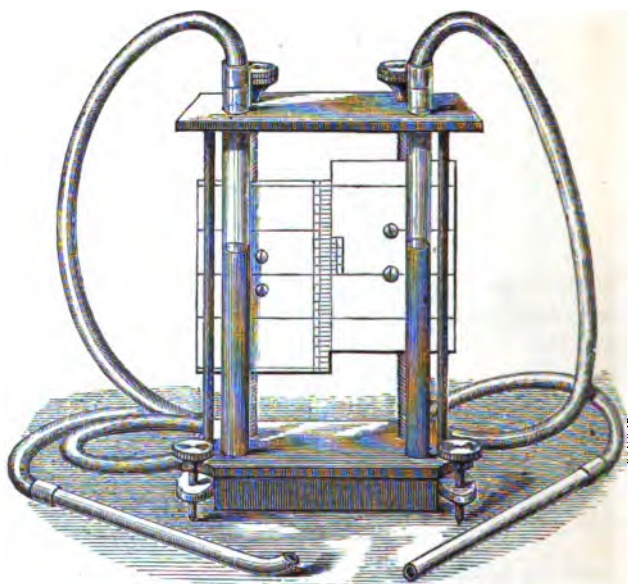


only adapted for currents of a greater speed than 5 feet per second. Fletcher overcame this difficulty thus:—In order to lessen the friction, he employed two cylinders, *a a'*, fig. 174, of 4 inches diameter, connected at the bottom by a narrow tube, *b*. This arrangement is ten times as sensitive as a U-tube of 0.4 inch width would be, since the area upon which the pressure acts is increased 100-fold, but the circumference upon which friction acts only 10-fold. The rising and falling of the liquid is observed by means of metal floats, *c c*, upon which a very fine horizontal line is marked by a lathe; and the scale, *d*, provided with a vernier and a very fine adjusting-screw, permits the difference of level, down to

one thousandth part of an inch, to be read off. This is possible, not with water, whose mobility, owing to its adhesion to the glass, is too slight, but with *ether*, whose adhesion is only one two-thousandth of that of water. The two glass tubes, *e* and *f*, are put into the draught-pipe, *k*, by means of a cork, *g*, at right angles to the current of gas (so that it blows into the bent tube, *f*), and are connected by elastic tubes, *h i*, with *a a'*.

The form of anemometer shown in fig. 174 has now been replaced by the simpler one shown in fig. 175. Lenses have

Fig. 175.



also been added to make the readings more accurate; but these, in my experience, give more trouble in making the observations than is gained by the greater accuracy of reading the scales.

In the original communication by Mr. Fletcher, as well as in the first edition of this work (pp. 333-335), we find the mathematical evolution of the laws for ascertaining the relation of the readings to the speed of the currents. We abstain from repeating this reasoning here, and merely give the final formula found for ascertaining the velocity of the gaseous current v from the height

of the column of ether (of 0.740 spec. gravity) = p , for any temperature t (in degrees Fahrenheit) and barometric pressure h (in inches) :—

$$v = \sqrt{p \frac{29.92}{h} \times \frac{519}{459+t}} \times 28.55.$$

The Table given on p. 439, for the speeds corresponding to different readings of the anemometer, is computed from the formula

$$v = \sqrt{p} \times 28.55;$$

and another Table is added for correcting the variations in the temperature of the current of gas. The corrections for small variations in the barometrical pressure are usually not considerable; but they can be made by means of the above formulæ—

$$v'' = \sqrt{p \frac{29.92}{h}} \times 28.55,$$

or

$$v = \sqrt{p \frac{h}{29.92}} \times 28.55.$$

If the pressure is read off in millimetres, the number 760 is everywhere substituted for 29.92; or if the readings are in millimetres and the speed in metres per second is required to be known, the constant 28.55 is converted into another, according to the formula

$$\frac{0.3048}{\sqrt{25.4}} \times 28.55 = 1.727;$$

so that the formula for v' and p' in metrical measures will read $v' = 1.727 \sqrt{p'}$.

A correction for the expansion and contraction of the ether in the instrument itself is mostly unnecessary, since it is only exposed to the ordinary temperature; it amounts to about 1 per cent. of the speeds shown in the Table for each 10°F. ($= 5.55^\circ \text{C.}$) deviation from 60°F. ,—more for temperatures below, less for temperatures above 60°F.

In order to make the readings more exact, first the height of ether in one of the limbs is noticed, then the current is reversed by connecting the tube e with a and f with a' (fig. 174); another reading is made; and thus twice the difference of pressure caused by the suction at f is found. The figure thus found is read off in

Table I. and corrected for temperature by Table II. To take an instance, let the first reading be 1·039, and the second reading, after reversing the current, 0·861, the difference will be 0·178. On referring to Table I., the speed 12·05 feet per second will be found. This, however, is only true if the temperature of the air is 60° F. Should it in the case in question be 520° F., Table II. gives the correcting multiplier, 0·7280. This, multiplied by 12·05, is 8·772, the true speed of the current if measured at the temperature of 60° F.

This instrument is not influenced by soot, heat, or corrosive vapours; it can be placed at some distance from the flue to be tested, if longer elastic tubing be used; and it can, of course, be employed both for aspirating and for pressure currents (fan-blasts &c.), and as a measure for the speed of atmospheric currents.

Of course, like every other anemometer, Fletcher's only indicates the pressure at the place occupied by its receiving portion; and accordingly the tubes *e* and *f* must be introduced so far as to reach into the air-current to the extent of about one sixth of the diameter of the flue. The velocity at this place is assumed to be nearly equal to the average; but this is very doubtful, and there are no means at present known of measuring the absolute quantities of air passing through a flue of any considerable sectional area with any degree of certainty.

ANEMOMETERS.

TABLE I.—*Showing the Speed of Currents of Air and Ether Anemometer.*

$$v = \sqrt{p \times 28.55}.$$

Temperature 60° Fahr. Barometer 29.9

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.
in.	ft. per sec.	in.	ft. per sec.	in.
0-001	0.903	0-047	6.189	0-001
0-002	1.277	0-048	6.255	0-002
0-003	1.564	0-049	6.320	0-003
0-004	1.806	0-050	6.384	0-004
0-005	2.019	0-051	6.448	0-005
0-006	2.212	0-052	6.510	0-006
0-007	2.389	0-053	6.572	0-007
0-008	2.554	0-054	6.634	0-008
0-009	2.709	0-055	6.695	0-009
0-010	2.855	0-056	6.756	0-010
0-011	2.994	0-057	6.816	0-011
0-012	3.127	0-058	6.876	0-012
0-013	3.255	0-059	6.935	0-013
0-014	3.378	0-060	6.993	0-014
0-015	3.497	0-061	7.051	0-015
0-016	3.612	0-062	7.109	0-016
0-017	3.723	0-063	7.166	0-017
0-018	3.830	0-064	7.223	0-018
0-019	3.935	0-065	7.279	0-019
0-020	4.038	0-066	7.335	0-020
0-021	4.137	0-067	7.390	0-021
0-022	4.235	0-068	7.445	0-022
0-023	4.330	0-069	7.500	0-023
0-024	4.423	0-070	7.554	0-024
0-025	4.514	0-071	7.608	0-025
0-026	4.604	0-072	7.661	0-026
0-027	4.691	0-073	7.713	0-027
0-028	4.777	0-074	7.766	0-028
0-029	4.862	0-075	7.819	0-029
0-030	4.945	0-076	7.871	0-030
0-031	5.027	0-077	7.922	0-031
0-032	5.107	0-078	7.974	0-032
0-033	5.187	0-079	8.025	0-033
0-034	5.265	0-080	8.075	0-034
0-035	5.342	0-081	8.125	0-035
0-036	5.418	0-082	8.175	0-036
0-037	5.492	0-083	8.225	0-037
0-038	5.565	0-084	8.275	0-038
0-039	5.638	0-085	8.324	0-039
0-040	5.710	0-086	8.373	0-040
0-041	5.781	0-087	8.421	0-041
0-042	5.851	0-088	8.469	0-042
0-043	5.921	0-089	8.517	0-043
0-044	5.989	0-090	8.565	0-044
0-045	6.056	0-091	8.613	0-045
0-046	6.123	0-092	8.660	0-046

TABLE I. (continued).

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0.178	12.05	0.284	15.23	0.390	17.83
0.180	12.11	0.286	15.28	0.392	17.88
0.182	12.18	0.288	15.33	0.394	17.93
0.184	12.25	0.290	15.38	0.396	17.98
0.186	12.31	0.292	15.44	0.398	18.02
0.188	12.38	0.294	15.49	0.400	18.06
0.190	12.45	0.296	15.54	0.402	18.11
0.192	12.51	0.298	15.59	0.404	18.16
0.194	12.57	0.300	15.64	0.406	18.20
0.196	12.64	0.302	15.70	0.408	18.24
0.198	12.71	0.304	15.75	0.410	18.28
0.200	12.77	0.306	15.80	0.412	18.33
0.202	12.83	0.308	15.85	0.414	18.38
0.204	12.90	0.310	15.90	0.416	18.42
0.206	12.96	0.312	15.95	0.418	18.46
0.208	13.02	0.314	16.00	0.420	18.50
0.210	13.08	0.316	16.05	0.422	18.55
0.212	13.15	0.318	16.10	0.424	18.60
0.214	13.21	0.320	16.15	0.426	18.64
0.216	13.27	0.322	16.20	0.428	18.68
0.218	13.33	0.324	16.25	0.430	18.72
0.220	13.39	0.326	16.30	0.432	18.77
0.222	13.45	0.328	16.35	0.434	18.82
0.224	13.51	0.330	16.40	0.436	18.86
0.226	13.57	0.332	16.45	0.438	18.90
0.228	13.63	0.334	16.50	0.440	18.94
0.230	13.70	0.336	16.55	0.442	18.99
0.232	13.76	0.338	16.60	0.444	19.03
0.234	13.82	0.340	16.65	0.446	19.07
0.236	13.88	0.342	16.70	0.448	19.11
0.238	13.94	0.344	16.75	0.450	19.15
0.240	13.99	0.346	16.80	0.452	19.20
0.242	14.05	0.348	16.85	0.454	19.24
0.244	14.11	0.350	16.89	0.456	19.28
0.246	14.17	0.352	16.94	0.458	19.32
0.248	14.23	0.354	16.99	0.460	19.36
0.250	14.28	0.356	17.04	0.462	19.41
0.252	14.34	0.358	17.09	0.464	19.45
0.254	14.40	0.360	17.13	0.466	19.49
0.256	14.45	0.362	17.18	0.468	19.53
0.258	14.50	0.364	17.23	0.470	19.57
0.260	14.56	0.366	17.28	0.472	19.62
0.262	14.62	0.368	17.33	0.474	19.66
0.264	14.68	0.370	17.37	0.476	19.70
0.266	14.74	0.372	17.42	0.478	19.74
0.268	14.79	0.374	17.47	0.480	19.78
0.270	14.84	0.376	17.52	0.482	19.82
0.272	14.90	0.378	17.56	0.484	19.86
0.274	14.96	0.380	17.60	0.486	19.90
0.276	15.01	0.382	17.65	0.488	19.94
0.278	15.06	0.384	17.70	0.490	19.98
0.280	15.11	0.386	17.75	0.492	20.02
0.282	15.17	0.388	17.79	0.494	20.06

TABLE I. (continued).

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0.496	20.10	0.590	21.94	0.700	23.89
0.498	20.14	0.600	22.12	0.750	24.73
0.500	20.18	0.610	22.30	0.800	25.54
0.510	20.38	0.620	22.48	0.850	26.32
0.520	20.58	0.630	22.66	0.900	27.08
0.530	20.78	0.640	22.84	0.950	27.83
0.540	20.98	0.650	23.02	1.000	28.55
0.550	21.17	0.660	23.20	1.250	31.93
0.560	21.37	0.670	23.38	1.500	34.97
0.570	21.56	0.680	23.55	1.750	37.77
0.580	21.75	0.690	23.72	2.000	40.37

TABLE II.—Showing the Values of $\sqrt{\frac{519}{459+t}}$ for Values of t from 0 to 1000; or Corrections for Temperature.

t , degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t , degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t , degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$
0	1.0634	130	0.9388	260	0.8497
5	1.0577	135	0.9348	265	0.8467
10	1.0520	140	0.9309	270	0.8438
15	1.0464	145	0.9270	275	0.8409
20	1.0409	150	0.9232	280	0.8380
25	1.0355	155	0.9194	285	0.8352
30	1.0302	160	0.9156	290	0.8324
35	1.0250	165	0.9119	295	0.8296
40	1.0198	170	0.9083	300	0.8269
45	1.0148	175	0.9047	305	0.8242
50	1.0098	180	0.9012	310	0.8215
55	1.0049	185	0.8977	315	0.8189
60	1.0000	190	0.8943	320	0.8163
65	0.9952	195	0.8909	325	0.8137
70	0.9905	200	0.8875	330	0.8111
75	0.9858	205	0.8841	335	0.8085
80	0.9812	210	0.8808	340	0.8060
85	0.9767	215	0.8775	345	0.8035
90	0.9723	220	0.8743	350	0.8010
95	0.9679	225	0.8711	355	0.7985
100	0.9636	230	0.8680	360	0.7960
105	0.9593	235	0.8649	365	0.7936
110	0.9551	240	0.8618	370	0.7912
115	0.9509	245	0.8587	375	0.7888
120	0.9468	250	0.8557	380	0.7865
125	0.9428	255	0.8527	385	0.7842

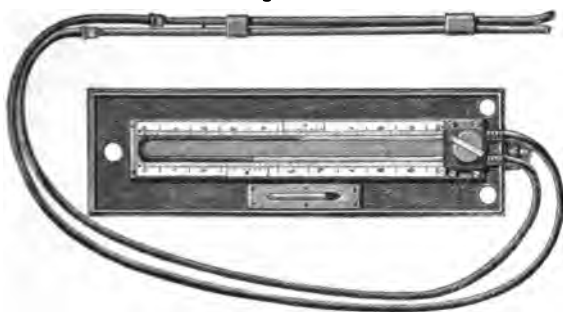
TABLE II. (continued).

t , degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t , degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$	t , degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$
390	0.7819	595	0.7017	800	0.6420
395	0.7786	600	0.7000	805	0.6407
400	0.7763	605	0.6983	810	0.6395
405	0.7741	610	0.6967	815	0.6382
410	0.7729	615	0.6951	820	0.6369
415	0.7707	620	0.6935	825	0.6357
420	0.7685	625	0.6919	830	0.6345
425	0.7663	630	0.6903	835	0.6333
430	0.7641	635	0.6887	840	0.6321
435	0.7619	640	0.6871	845	0.6309
440	0.7598	645	0.6856	850	0.6297
445	0.7577	650	0.6841	855	0.6285
450	0.7556	655	0.6826	860	0.6273
455	0.7535	660	0.6811	865	0.6261
460	0.7514	665	0.6796	870	0.6249
465	0.7494	670	0.6781	875	0.6237
470	0.7474	675	0.6766	880	0.6225
475	0.7454	680	0.6751	885	0.6214
480	0.7434	685	0.6736	890	0.6203
485	0.7414	690	0.6721	895	0.6192
490	0.7394	695	0.6706	900	0.6181
495	0.7375	700	0.6691	905	0.6169
500	0.7356	705	0.6676	910	0.6158
505	0.7337	710	0.6662	915	0.6147
510	0.7318	715	0.6648	920	0.6136
515	0.7299	720	0.6634	925	0.6125
520	0.7280	725	0.6620	930	0.6114
525	0.7261	730	0.6606	935	0.6103
530	0.7243	735	0.6592	940	0.6092
535	0.7225	740	0.6578	945	0.6081
540	0.7207	745	0.6565	950	0.6070
545	0.7189	750	0.6552	955	0.6059
550	0.7171	755	0.6538	960	0.6048
555	0.7153	760	0.6524	965	0.6037
560	0.7137	765	0.6511	970	0.6026
565	0.7119	770	0.6498	975	0.6015
570	0.7102	775	0.6485	980	0.6004
575	0.7085	780	0.6472	985	0.5994
580	0.7068	785	0.6459	990	0.5984
585	0.7051	790	0.6446	995	0.5974
590	0.7034	795	0.6433	1000	0.5964

Fletcher's anemometer has been improved by Swan in the following way, practically returning to Péclet's original construction (a similar plan has been independently proposed by P. Hart, Chem. News, vol. xxi. p. 200). In lieu of the 4-inch cylinders he takes a U-tube of $\frac{1}{8}$ inch diameter, narrowed in the bend to diminish the oscillations. The tube is 10 inches long, and placed with an inclination of 1 in 10; each limb has a scale and vernier,

the latter partly made of glass and covering at the same time the scale and the tube, so that it is easy to read off to $\frac{1}{100}$ inch. The ends of the tube are connected with a two-way cock, so that the current can be reversed without opening any joint. Fig. 176 shows the instrument as seen from above, so that its inclination

Fig. 176.



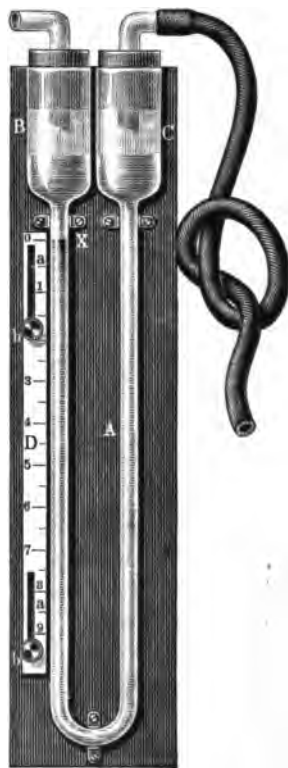
to the vertical line does not appear. It is fixed on a stand provided with a spirit-level and adjusting-screws. It is employed just like Fletcher's anemometer; but, owing to the inclination of 1 in 10, the column of ether in the tube occupies ten times the space corresponding to its height, and the reading to $\frac{1}{100}$ inch gives thus the same result as the very difficult one to $\frac{1}{1000}$ inch in Fletcher's instrument. The narrowness of the tubes does not matter in the case of ether, as the friction may be entirely neglected with this substance (the later form of Fletcher's anemometer, shown in fig. 175, bears this out as well). Swan's anemometer must always be placed exactly level in the direction of its length; but it need not be levelled across, if a reading be made in one limb, the two-way cock turned, and the new reading in the same limb subtracted from the first; thus it is unnecessary to read off at both limbs, which would involve levelling across as well. The speeds are found from Fletcher's table, dividing the readings by 10. (The value of this improvement is doubtful, as it is not possible to read off the standing surface of the ether in the inclined tube with anything like the accuracy attainable in a vertical tube. Compare also the similarly constructed pressure-gauge shown on p. 397.)

Other instruments for measuring the draught are, for instance, those of Kretz (Dingl. Journ. cxc. p. 16), of Ramsbottom (ib.

clxxx. p. 334), of Scheurer-Kestner (ib. ccvi. p. 448 and ccxi. p. 427), none of which can vie with Fletcher's in sensitiveness. The very ingenious anemometer of Hurter (Dingl. Journ. ccxxix. p. 160) is only adapted for laboratory use. Compare also Bourdon's multiplying anemometer (Compt. Rend. vol. xciv. p. 5; Journ. Soc. Chem. Ind. 1882, p. 60).

One of the most delicate anemometers is Fryer's, described in the Inspector's Report on the Alkali Acts for 1877-78, p. 68. Its principle is to measure the difference of pressure on each side of a watch-glass shaped copper plate, connected with a spiral spring. It will measure a pressure of $\frac{1}{3000}$ of an inch.

Fig. 177.



Recently differential anemometers on another principle have come into use very largely, and seem to be preferable to all others. There are already a good many forms of this apparatus, one of the

best known being that of Professor Seger (G. P. 19426) and shown in fig. 177. The calibrated U-tube A is surmounted by two cylindrical cups, B and C, of equal width. The board on which it is fastened also carries the sliding scale D, adjustable by slits *a a* and screw-pins *b b*. The tube is filled with two not miscible liquids, for instance heavy paraffin oil and dilute, coloured spirits of wine, of nearly equal specific gravity, in such manner that the zero-point of the scale D can be put exactly at the line of contact of both liquids at X. If an aspirating force is acting on the surface of the liquid in C, which raises the level in that part of the tube, the point X will be lowered at a multiplied ratio, corresponding to the difference in the sectional area of the narrow part of A and the enlargement in C. If, for instance, the ratio of the sections is as 1 to 20, a difference of pressure of 1 millimetre will be indicated on the scale by a sinking of X to the amount of 20 millimetres. The scale is graduated in such a way that it indicates the pressure, expressed in millimetres of water. This instrument is much cheaper and easier to handle than those constructed on Péclet's principle and quite as accurate.

*Calculation of the Volume of Chamber-Gases according to
Temperature and Moisture.*

In all calculations concerning chamber-gases it is not sufficient to take into account the difference of temperature and barometric pressure from the normal state of 0° and 760 millim., but the amount of moisture present in the chamber-atmosphere must be equally brought into the calculations. It is evidently impossible to do this on the assumption that the tension of aqueous vapour within the chambers is that ordinarily existing for any given temperature; the presence of sulphuric acid, not merely at the bottom but all over in the shape of mist, greatly changes the aqueous-vapour tension according to the varying strength of the acid. The tables of Regnault and Sorel, given on pp. 136 and 137, would admit of making the calculation in the proper manner; but it will be more convenient to consult the following Table, p. 446 (calculated by Sorel), which immediately gives the *volume occupied by a cubic metre (or cubic foot) of air, originally at 0° C. and 760 millimetres pressure, after being brought into equilibrium of temperature and vapour-tension with dilute sulphuric acid of varying strength and temperature, but without any change of pressure.*

Percentage of H_2SO_4 in the acid.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.	80°.	85°.	90°.	95°.
44	1.042	1.063	1.085	1.108	1.133	1.160	1.192	1.225	1.263									
46	1.042	1.062	1.084	1.107	1.131	1.157	1.188	1.218	1.256	1.303	1.356	1.427						
48	1.042	1.062	1.083	1.105	1.129	1.155	1.185	1.212	1.249	1.292	1.341	1.397	1.478	1.542				
50	1.041	1.061	1.082	1.104	1.128	1.152	1.180	1.207	1.241	1.281	1.327	1.377	1.452	1.509	1.589	1.756	1.911	
52	1.041	1.060	1.081	1.103	1.125	1.150	1.177	1.202	1.234	1.270	1.313	1.359	1.429	1.478	1.562	1.662	1.830	2.014
54	1.040	1.060	1.080	1.102	1.122	1.147	1.175	1.198	1.227	1.260	1.301	1.343	1.408	1.449	1.526	1.625	1.752	1.904
56	1.040	1.059	1.079	1.100	1.121	1.144	1.169	1.194	1.222	1.252	1.290	1.328	1.388	1.423	1.490	1.589	1.684	1.813
58	1.039	1.059	1.078	1.099	1.120	1.142	1.166	1.190	1.215	1.244	1.279	1.313	1.369	1.400	1.456	1.534	1.625	1.734
60	1.039	1.058	1.077	1.098	1.119	1.140	1.163	1.186	1.209	1.237	1.269	1.290	1.352	1.368	1.428	1.495	1.575	1.688
62	1.038	1.058	1.077	1.097	1.118	1.138	1.160	1.182	1.204	1.230	1.261	1.289	1.335	1.357	1.402	1.462	1.532	1.613
64	1.038	1.057	1.076	1.096	1.117	1.136	1.158	1.178	1.200	1.224	1.253	1.279	1.322	1.337	1.379	1.431	1.493	1.562
66	1.038	1.057	1.076	1.095	1.116	1.135	1.157	1.175	1.197	1.219	1.246	1.271	1.311	1.324	1.362	1.408	1.464	1.522
68	1.038	1.056	1.075	1.095	1.114	1.134	1.156	1.173	1.194	1.215	1.239	1.263	1.302	1.316	1.347	1.388	1.437	1.488
70	1.038	1.056	1.075	1.094	1.114	1.133	1.155	1.172	1.192	1.212	1.235	1.258	1.293	1.308	1.338	1.386	1.412	1.456
72	1.038	1.056	1.074	1.094	1.113	1.132	1.153	1.171	1.191	1.210	1.232	1.254	1.289	1.302	1.330	1.344	1.391	1.429
74	1.037	1.056	1.074	1.093	1.112	1.131	1.152	1.170	1.190	1.209	1.229	1.251	1.284	1.296	1.321	1.340	1.374	1.407
76	1.037	1.055	1.074	1.093	1.111	1.131	1.151	1.169	1.189	1.208	1.227	1.248	1.280	1.291	1.313	1.337	1.362	1.388
78	1.037	1.055	1.074	1.092	1.111	1.130	1.150	1.168	1.188	1.207	1.226	1.246	1.277	1.287	1.307	1.330	1.352	1.376
80	1.037	1.055	1.073	1.092	1.110	1.130	1.149	1.167	1.187	1.206	1.225	1.245	1.275	1.284	1.303	1.324	1.346	1.367
82	1.037	1.055	1.073	1.091	1.110	1.129	1.149	1.166	1.186	1.205	1.224	1.244	1.274	1.283	1.300	1.318	1.339	1.359

CHAPTER VII.

THE CHAMBER-PROCESS.

Starting the Chambers.

IN order to *start a set of chambers*, first of all the chamber-bottoms must be covered with acid. This is absolutely necessary when the sides are not burnt to the bottom, but hang loosely down into its upstand, as here an hydraulic lute is required to keep the gas within the chamber. Enough liquid for the sides just to dip into it is sufficient; for as the lead expands on the chamber getting warm, and as the liquid constantly increases by condensation, the hydraulic lute is constantly improving. However, for reasons to be stated hereafter, it will be preferred to make the depth of acid as great as possible from the outset. Only in extreme cases ought *water* to be taken for luting the chamber; acid should rather be bought elsewhere at some expense to avoid this. If it can be done, the proper thing is to bring up the bottom-acid at once to about 90° Tw. If this cannot be done, this strength ought at least to be approached as nearly as possible. The reason why starting a chamber with water or very weak acid should be avoided is, that otherwise the vapour of nitric acid dissolves in the bottom-liquid and acts upon the lead.

Even if all the nitric acid freshly supplied were decomposed by sulphurous acid before reaching the bottom, the presence of water or very dilute acid in large quantity would cause the new formation of large quantities of nitric acid from all the lower oxides of nitrogen (N_2O , N_2O_3 and NO), and, on the other hand, of nitrous oxide, N_2O ; there would thus be a large loss of nitre in both shapes, apart from the action of the lead, and the reactions within the chamber would be quite irregular. Altogether the chamber-process only goes on properly when there is an abundant quantity

of pretty strong acid at the bottom of the chambers. If the sides are burnt to the bottom, it is even preferable to start a chamber dry to starting it with water; but otherwise a layer of about 4 inches of acid on the bottom of such chambers is preferred.

Supposing the chambers to be luted with acid, and the burners to be heated up so that they can be charged, the connection between them and the chambers is made and the burner-gas allowed to enter. Of course sufficient draught is given and nitric acid admitted at once, but at first no steam, in order not to dilute the bottom-acid too much. The nitric acid is introduced precisely in the same way as later on, either in the gaseous or liquid form. At first about three or four times as much is put in as is necessary afterwards, because there must be a stock of nitre-gas collected in the chambers, which afterwards needs only to be renewed so far as any loss is suffered. Liquid nitric acid can be introduced much more quickly than gaseous, since the latter depends upon the heat of the burner-gas working the nitre-oven; but with liquid acid the thing must not be overdone, since it might not be decomposed entirely before reaching the bottom. This can hardly happen when introducing it through the Glover tower. At the beginning from 12 to 15 parts of nitrate of soda, or a corresponding quantity of nitric acid, will be employed to 100 parts of sulphur; and this will be continued till the last chamber turns yellow; then the quantity is gradually diminished till the proper point is reached.

MacCulloch (Chem. News, xxvii. p. 136) prescribes starting chambers by admitting steam and nitre-gas from the steam column (comp. the next Chapter) for five or six hours before the burner-gas is admitted. In that case, he says, the chamber works well from the first, and in one instance showed acid of 1.65 at the drips already in 12 hours. This may be so; but that process, while saving a little time and possibly a little nitre, from the outset detracts much from the durability of the chambers, since during the five or six hours when they receive only steam and nitre-gas very much nitric acid must condense, and whatever is gained by the drips is again lost by the previous dilution of the bottom-acid.

As soon as the drips and test-plugs prove that sulphuric acid is already forming in the chamber, steam is admitted, usually on the second day, but at first with much caution. Then all the factors

of vitriol-making are at work, and the same rules are now valid as for the ordinary process. If every thing is in proper order, and if plenty of nitre is used (none of which, with a Gay-Lussac tower, is lost), a chamber may be in regular working order on the fourth, sometimes even on the third day after starting.

We must also take into account the opposite case, that *when a set of chambers has to be stopped for repairs*. It may be necessary to do so for one or two days, and it is, of course, most important to be able to go on again as quickly as possible, without losing too much nitre. If the proper precautions are neglected, it is possible that so much nitric acid is produced that the chamber-lead is seriously acted upon. To avoid this, we must proceed as follows:—First of all, the pyrites-burners are stopped; no fresh charge is put in, and all openings are closed as tightly as possible. Next to this the supply of nitre is stopped, but that of steam is continued, so long as the gas of the last chamber shows any outward pressure. When this has ceased, and there is on the contrary some inward suction, the outlet damper is closed, and air is allowed to enter at some lute, manhole, sight, &c., to avoid forcing in of the chamber-walls by the atmospheric pressure. Even now there is a good deal of acid produced, as proved by the action of the drips; but the steam should be shut off as soon as the drips go down to 100° Tw. When the drips cease to act all openings are shut. If the burners are started again within three days from the stoppage, it is only necessary to put on a good supply of nitre in order to get the chambers to work again; the regulation of the steam must, however, be as carefully attended to as when starting a new set of chambers.

Supply of Air.

The object of a regular chamber-process is of course this:—to make from a given quantity of brimstone or pyrites the greatest possible quantity of sulphuric acid with the smallest possible consumption of nitre. We may add at once, as less decisive, but still of importance, to make the chamber-acid as strong as is compatible with the two conditions just stated and with a saving of the chamber-lead. In order to attain that object, the attention of the chamber-manager must be directed to many points, some of which have already been treated of in detail, whilst others must be enlarged upon here.

1st. *Complete Combustion of the Sulphur-ore.*—This, with brim-

stone, follows as a matter of course ; with pyrites it is much more difficult (compare about this p. 232 *et seq.*).

2nd. *Proper Composition of the Burner-gas.*—This also has been treated of in the 5th Chapter ; and we will here merely repeat that the proper composition of the burner-gas almost entirely depends upon the regular supply of air produced by proper regulation of the *draught*. We have already seen (p. 239) that, apart from chemical analysis, there are practical tests to show at the burners whether the draught is right or not. But at the chambers themselves this must equally be looked to, by means of the man-lids in the top, or the test-plugs (p. 397), or by pressure-gauges or anemometers (pp. 397 and 434). Generally, the following rules may be laid down as a rough guidance :—

In a set of three chambers the first chamber should show an outward pressure, and, accordingly, the gas should issue in force whenever a plug is opened. In the middle chamber the gas should be pretty nearly in equilibrium with the outer air ; in any case there should be rather a little outward pressure than any inward suction. In the last chamber there should be some, but very little, inward suction ; and behind it, but before the damper, the suction should be very perceptible. Knapp compares the chambers to a lake traversed by a river : the speed of current at its inlet is diminished in the interior of the wide basin so as to be almost imperceptible ; but at the outlet in the narrow draught-pipe it again comes out with the same strength as at first. Payen's '*Précis*' (i. p. 318) states the speed of the gas within the chambers to be 8 to 10 inches per minute.

Generally, it may be said that the draught must be sufficient to obtain a proper working of the burners and proper composition of the gas, but *no more than this*. In England this was formerly observed merely by practical indications, in Germany quite as generally by testing the burner-gas for SO_2 , and the exit-gas for O, and this is now frequently done in England as well. The rule given can here be stated more precisely in this form :—There is so much draught given that the burner-gas from brimstone approaches a percentage of 11 per cent., that from pyrites 8 per cent. SO_2 , as far as circumstances permit, and that the gas issuing at the end still contains 5 or, better, 6 per cent. of oxygen.

Too much draught causes, with brimstone, a sublimation of the same ; with pyrites also too rapid a combustion, and consequently a formation of scars. If very high, it produces cooling by the inert

excess of air, also poor gas, defective utilization of the chamber-space, aspiration of air through all chinks of the chambers, carrying away of sulphurous acid and of nitrogen oxides.

Insufficient draught causes the burners to become too hot, the formation of scars, incomplete burning of the ore (and consequently again poor gas), blowing out of the burners, connecting-pipes, and chambers from all crevices (especially when any working-doors are opened), insufficient oxidation of sulphurous acid within the chambers, and escape of nitre-gas because the oxygen for forming absorbable nitrogen oxides is not present.

Either causes (as a consequence of the above) a bad yield of vitriol, large consumption of nitre, escape of sulphurous acid into the air. Further proof is not required to show the importance of regulating the draught as accurately as possible.

In the case of poor ores, and those the sulphur of which is not readily given off, also in the case of burners admitting too much false air, such as the old Belgian burners, too much air gets into the chambers, and the yield is consequently always very bad. At Oker, for instance, in 1859, from a 50-per-cent. pyrites only 100 instead of 300 per cent. of strong vitriol was obtained, with a consumption of 14.4 parts of nitre to 100 sulphur (Knocke, in Wagner's *Jahresb.* 1859, p. 148); and the Belgian Commission states, for the four works examined, the yield = 242, 237, 259, and 238 parts, instead of 306 as required by theory. They were able to detect in the escaping gas 0.38 to 1.26 per cent. of sulphurous acid, and 11.7 to 17.4 per cent. of free oxygen.

The regulation of the draught takes place principally or sometimes even exclusively at the exit end by means of the contrivances described (p. 428 *et seq.*). It is not practicable to depend for this entirely on the ash-pit holes of the pyrites-burners (pp. 239 and 240), as these must be regulated to suit each individual burner. It is very important not to overlook that the gas-pipe between the burners and the Glover tower and the chamber may be partially stopped up with deposit. In this case the draught at the burner will be bad, but will be little improved by opening the exit damper ever so wide, and closing the latter will only draw in air at any chance crevice and injure the chamber-process. This cannot be overlooked if the process is properly controlled by regularly testing the burner-gas and exit-gas; if the latter shows enough or more than enough free oxygen while the burner-gas is blowing out, there must be some intermediate stoppage. The lutes or side-

plugs, or still better simple pressure-gauges (p. 397) fixed in various places of the set, will easily allow of localizing that stoppage.

On the contrary, as we have seen on p. 428, some prefer working in this way, that there is always *ample* draught from the burners into the first chamber, by employing large and very loosely-packed Glover towers; the burners in this case never blow out, and yet the chambers themselves can be worked right to the end, with even outward pressure in lieu of inward draught. But there must then be this drawback that, owing to the loose packing, the denitration in the Glover tower will be hardly perfect. This can be obviated by the following plan, which may be usefully adopted in special cases. The Glover tower is packed as usual, so as to be an efficient denitrator and concentrator. From it the gases are still made to ascend a sufficient height, say 6 or 10 feet, in a wide tube, which then turns (avoiding any sharp bends) sideways and dips down into the roof of the first chamber. Thus a siphon is formed, and as the gases in the second, descending limb are cooler than in the part rising upwards from the tower (in extreme cases the air-cooling might even be supplemented in summer by water-cooling), this will cause suction of the gases from the tower, and thus increase the draught from the burners, without drawing the gas away from the chambers too quickly at the other end.

Exceptionally, air is admitted behind the burners, usually by means of an injector in the first chambers which is so constructed as to introduce some air along with the steam (p. 429). This must be done where the burner-gases are too rich, and especially where the first supply of air is purposely kept as low as possible, in order to get hotter gas, as, for instance, in H. Glover's brimstone-burner (p. 201), which is intended to concentrate the acid by the heat of the gases.

Some chamber-managers contend that no regulation of the draught need take place at the outlet when this has been done once for all, as the outside atmospheric conditions are never so varying as to interfere with the working of the process. But this opinion is decidedly wrong. In most parts of Central Europe the temperature may vary up to 40° C., or even more, between the extreme heat of summer and the extreme cold of winter. But this means that for every 1000 cubic feet of air required in the coldest season, nearly 1150 cubic feet must pass through the apparatus in

the hottest season, supposing the barometric pressures to be equal. But these latter as well may vary 30 millimetres, or even more; so that, for instance, 1000 cubic feet at 760 mm. pressure represent the same weight of air as 1041 cubic feet at 730 mm. Combining both (and very frequently low temperatures and high barometric pressure go together, as well as high temperatures and a low barometer), 1000 cubic feet in winter may be equal in weight to 1200 cubic feet in summer. It is quite evident that such large differences, and even much lesser ones, as they may occur from day to day, *must* be compensated by regulating the outlet of the gases accordingly. Nor must it be overlooked that the pressure of wind affects the quantity of gases passing through a given orifice, and this circumstance sometimes in the year has a very serious effect on the draught, even when the burner-house (as it ought to be) is sheltered against the direct action of gusts on the ash-pits.

Supply of Water (Steam).

The regulation of the steam is one of the most important parts of chamber-management, and should always be taken in hand by the responsible foreman or superintendent himself. One of the first conditions for enabling him to do so properly is that the tension of the steam should be kept as nearly equal as possible; and it is hardly necessary to point out how much this task is facilitated by a registering steam-gauge or by automatically regulating steam-valves (pp. 416, 417). The round of the chambers should be made two or three times a day; at some works it is even made every other hour. It is one of the advantages of the water-spray system (p. 421) that there are hardly any variations of the quantity of water supplied, but other difficulties may occur instead (p. 424).

It must be borne in mind that the Glover tower supplies the first or "leading" chamber of a set with a good deal of the steam required. Hence steam or water-spray must be supplied to this chamber in much less quantity than when working without a Glover tower, and the position of the jets is also influenced by this (comp. p. 418).

A rough indication, whether too little or too much steam is present, is sometimes sought in the appearance of the glass jars covering the top-lutes of the chambers (p. 397). If these show a white crystalline covering of chamber-crystals, which are proved

as such by turning green on moistening them, there is evidently a deficiency of steam. If, on the other hand, the glass jars are dripping wet, there is too much steam in the chamber. This is, of course, only to be taken in conjunction with the other observations to be made by the attendant.

The proper indicator for the admission of steam or water is the *strength of acid made in the chamber*, both as observed in the acid-drips (p. 395) and in the bottom-acid. These two are never identical; the drip-acid is always more or less strong than the bottom-acid. In long chambers there is a considerable difference between the front and the back part, and such chambers should be provided with two or even more different sets of drips.

Considerable difference of opinion exists as to the strength of acid most conducive to a proper working of the vitriol-chambers, that is, to the best yield, the greatest production for a given chamber-space, and the smallest consumption of nitre. We may say generally that the chamber-acid is kept much stronger in the great majority of English works than in the majority of Continental works. Whilst the former mostly keep the acid in the leading chamber from 120 to 130 and the drips often 5 to 10 degrees higher, the usual practice on the Continent is to keep it at 106° to 110°, or at most 113° Tw. (the last is the usual strength in France). In America I found from 112 to 116 degrees. Only exceptionally higher strengths (up to 124° Tw.) are met with on the Continent or in America.

It is unnecessary to say that both English and Continental manufacturers firmly believe that they are in the right, the former in making stronger, the latter in making weaker chamber-acid. Both contend that in their, and only in their way the best results are obtained. It is difficult, if not impossible, to arrive at any certain judgment on the question from a comparison of the data supplied by various works as to the strength of acid, the yields, the consumption of nitre, the chamber-spaces, and so forth. This difficulty arises both from the complication of the various conditions, which interact upon one another, and from the very frequent inaccuracy and incompleteness of the obtainable figures. It is therefore with all reserve if I proceed to give my own opinion on this question (which differs from that given in the first edition of this work, vol. i. p. 346).

All *theories* of the vitriol-chamber process seem to point to the

preference of the *weaker* rather than of the stronger acid. Hurter, in his dynamical theory (J. Soc. Chem. Ind. 1882, p. 10) arrives at the result that the chamber-space is inversely proportional to the quantity of nitrogen compounds present, and to the amount of water present in the gaseous condition; in other words, that, other conditions being equal, the quantity of acid produced within a given chamber-space is larger when weaker acid is made than when strong acid is made. It is true that the evidence given for this in the paper just mentioned from the actual results of a number of chambers is very scanty, and certainly not sufficiently conclusive in itself; this was unavoidable, as only such works could be quoted which do not possess Gay-Lussac and Glover towers. But, at all events, no contrary assertion can be based on that evidence.

The theory propounded by myself, and the very similar one of Sorel, both of which will be found in Chapter IX., equally demand that, other conditions being equal, the vitriol-forming reaction is promoted by a larger amount of water, up to the limit where an excess of water would produce other, injurious, reactions.

Another point to be considered is this, that it is practically impossible to prevent the loss of some nitre, dissolved in the chamber-acid as nitroso-sulphuric acid, but that the tendency of the chamber-acid to retain nitre in this form rapidly increases with its strength. Theory would therefore demand keeping the acid weaker in order to lose less nitre. Whether this is so or not in practice could only be proved by bringing together a great many *reliable* data, the difficulty of doing which has been pointed out before. It is a *fact* that sometimes "pale" chambers are the consequence of giving too little steam, that is, keeping the acid too concentrated, and that this evil can be remedied by turning on full steam for a short time, when the chamber will become red again.

The practice of most Continental factories, including several German and Austrian works, at which all the processes are followed up in the laboratory with the greatest care, and which are generally admitted to work with the greatest perfection, is in accordance with the just-quoted theories, and comes to this: that the acid in the leading-chamber, that is at the same time that which is withdrawn from the process for use or sale, should not exceed 113° , and is best kept at from 106° to 110° Twaddell. Thus the best yield and the smallest consumption of nitre is attained.

The usual, and practically the only reasonable motive of English

manufacturers for making their chamber-acid so much stronger is, of course, this, that they save the expense and trouble of concentrating the acid for use or sale. But there is little or nothing in this in the great majority of cases. For the manufacture of superphosphates, which requires an enormous quantity of vitriol, and for which many vitriol-works are exclusively employed, the strength of 110° Tw. is quite sufficient. For decomposing salt for sale and for making rectified oil of vitriol a higher strength is certainly required. But at every works provided with Glover towers, that is, at every properly equipped works and actually in the great majority of existing factories, there is no difficulty whatever in bringing all the acid up to 140° Tw. without any expense, even when starting from chamber-acid at 110° Tw.; and this is done even without Glover towers (for further concentration in platinum stills) at many works by means of the waste heat of the pyrites-kilns.

Some years ago, P. W. Hofmann (Ber. d. deutsch. chem. Ges. iii. p. 5), starting from the (erroneous) assumption that sulphurous acid in contact with nitric acid and sulphuric acid of, say, 100° Tw., produced much nitrous oxide, N_2O , proposed to diminish the steam in the first chamber (which in his case was only a "tambour" of 3500 cubic feet capacity) to such an extent that acid of 140° Tw. should be formed; in this way the acid dissolves much nitre, and is run into the following large chamber, where it gets diluted and gives up the nitre. He asserted that he had thus effected a saving of 1 lb. nitre on 100 lbs. of sulphur; but as his original consumption of nitre and the yield are not stated, and as, moreover, his chambers had no Gay-Lussac and Glover towers, that alleged saving cannot convey any proof of the utility of his proposal, upon which a vivid controversy was raised in the 21st volume of the 'Chemical News' (pp. 132, 164, 189, 200, 224). It was then mostly overlooked that Hofmann's small "tambour" of 3500 cubic feet capacity had very little in common with an ordinary English leading chamber of more than ten times that capacity. Apart from all other reasons, the undoubtedly much greater wear and tear of the chamber, when worked in the described way, would tell much less with a small "tambour" than with a large chamber. But for the reasons above stated, Hofmann's process seems wrong in principle, and has not met with any success whatever on the Continent, where it was first tried.

In England recently (since 1889), probably without any reference to Hofmann's proposal of 1867, several works in Lancashire have begun to work with much stronger acid in the leading chamber, up to 140° Tw. It is, of course, out of the question to lose the nitre dissolved in such strong acid; none of it must be used without first passing through the Glover tower, and as it would become too strong therein, and would be incompletely denitrated, a little water is run through the tower at the same time. At one of the works visited by me it was stated that, with the very low chamber-space of 17 cubic feet per lb. of sulphur, the excellent yield of $41\frac{1}{2}$ cwt. of 96 per cent. salt-cake was obtained per ton of pyrites, with the very small consumption of 15 lbs. nitre per ton of pyrites ($=0.67$ per cent.). These good results were ascribed, firstly, to an extraordinarily large Gay-Lussac space; secondly, to the above procedure, by which an unusually large quantity of nitre was supposed to be kept circulating in the vitriol-chamber. It was not denied that there was more wear and tear of the chambers; but it was believed that this was no more than would be compensated by the saving in the process.

At the time of my visit to the above and a few other works, where the same method was followed, the process had not been sufficiently long in use to enable a correct judgment to be formed as to the yield and the consumption of nitre. Everybody knows that it requires many months to make sure of this, and to avoid any accidental gains and losses. But even taking it for granted that the above-quoted excellent results were really confirmed in the long run, I am very strongly disposed to place these results rather to the credit of the colossal Gay-Lussac towers, of a width of 14 feet and a height of 60 feet, than to that of keeping the chamber-acid at the dangerous strength of 140° Tw. It is clear that the large quantity of nitre kept in solution in the strong acid of the leading chamber can contribute but very little to the work of oxidizing sulphurous into sulphuric acid; its work can be done only whilst running down the Glover tower. But then the same object can be obtained quite as well, while keeping the chamber-acid at a lower strength, by supplying the Glover tower with more nitre, either (once for all) in the shape of nitric acid, or (continuously afterwards) in that of nitrous vitriol from the Gay-Lussac tower; the inert stock of nitre at the bottom of the

leading chamber is thus very largely reduced, and the confessedly much greater wear and tear of this chamber and of the Glover tower is thus avoided. From all indications it is also likely that less chamber-space will be required in this than in the former case.

It is difficult to say anything general on the strength at which the *drips of the first chamber* ought to be kept. At one works the drip-acid is only 2 or 3 degrees, at others 15 degrees or more above the bottom-acid; at others it is always weaker than the bottom-acid. Everything depends on the position of the drips; but so much is certain, that in the same plant the difference between the strength of the drip-acid and that of the bottom-acid is nearly constant, and that the attendant must manage his chambers accordingly. On the average, the drips where they are taken from the inside, clear of the chamber-sides, show about 10° Tw. more than the bottom-acid; but this holds good only with the ordinary style of working, not with that described above, where the bottom-acid is kept at 140° Tw.; in this case the drips are not very much or not at all stronger; and where the drips are collected at the chamber-sides they are generally somewhat weaker than the bottom-acid.

We have seen above (p. 136) that the tension of aqueous vapour varies both with the temperature and with the strength of the acid; for instance, at 80° (near the chamber-side), acid of 114° Tw. has exactly the same vapour-tension as, at 95° (only $2\frac{1}{2}$ inches within), acid of $128\frac{1}{2}^{\circ}$ Tw. Sorel observed that the acids collected at various points of the same transverse section of the chamber really showed such differences of strength, and that, therefore, it may be said that they are all at an equilibrium of aqueous-vapour tension. This shows how useless it is to compare the drips of different sets of chambers, unless they are fixed in a precisely similar way to one another.

The strength of acid in the intermediate chambers, between the first and the back chamber, is always below that of the first chamber. The second chamber, in a set of three, has generally about 10° Tw. less than the first; but with acid of 140° Tw. in the first chamber the difference between this and the second may amount to twice as much. In a set of four or more chambers the strengths will naturally diminish more gradually.

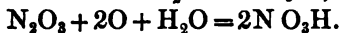
The last or "back" chamber is kept at very different strengths,

according to whether there is a Gay-Lussac tower connected with it or not. In the latter case the acid is never kept above 75° , and sometimes as low as 50° Tw., or even less than that. It is, in fact, difficult to keep the strengths higher, as there is so little sulphurous acid present, and as there must not be a large quantity of nitre, in order to avoid losing an enormous proportion of it. Thus there is but little acid made here, and it is correspondingly weak. But such weak acid, even at 75° , causes the formation of much nitric acid, which must act on the chamber-lead and is otherwise injurious. Hence with the old style of working without nitre-recovery apparatus, the last chamber was always a very weak link of the set.

In the presence of a Guy-Lussac tower, which is mostly used now, there is no reason whatever for keeping the last chamber below 90° Tw., or even a few degrees above this. There will be no formation of nitric acid to be apprehended in this case, and the gases will be better dried in preparation for the Gay-Lussac tower. The practice of some works to go down as low as 75° or 80° Tw. in the back chamber cannot be at all recommended.

We shall now describe *the evil consequences of a wrong supply of water* (as steam or spray) to the chambers.

The first and most obvious consequence of giving *too much steam* is this, that the acid gets too weak. But this is a minor affair compared to what follows immediately. If the lower oxides of nitrogen meet with an excess of oxygen (which is always present in the chambers) *and at the same time with an excess of water*, the following reactions take place:—



That is to say, they are converted into nitric acid, which, in the first instance, is a much less efficient carrier of oxygen than nitrous acid, and, secondly, is to a great extent dissolved in the bottom-acid; here it assists the acid-forming process very little and, moreover, acts upon the lead. So long as the bottom-acid is pretty strong (say, up to 90°), it will not long keep the nitric acid, but again give it off as lower nitrogen oxides by the action of sulphurous acid; but if the excessive supply of steam continues, it will soon keep the nitric acid back; and as the process is

thereby disturbed, even the steam * which should have been used up in the formation of sulphuric acid is condensed to water, and the dilution of the bottom-acid thus again increased. If this state has once set in, it is not always easily remedied. Cutting off the steam is not sufficient; much more nitre must be put in as well; and yet the bottom-acid only gradually gets up to its normal strength. In the meantime the yield falls off, the consumption of nitre increases very much, and the action on the chamber-lead does permanent damage. Thus it is apparent that an excess of steam does very much harm; and great care must be taken lest the strength of the acid should go down below the proper amount. The chambers soon show when they have too much steam by getting pale. A pale chamber often gets red again in an hour after the supply of steam has been partially cut off.

An excess of steam has another injurious consequence, which can only be explained in detail when treating of the theory of the chamber-process, viz. the formation of nitrous oxide, or even of nitrogen, whilst the reduction of the nitrogen-acids ought not to go beyond nitric oxide. Neither nitrous oxide nor nitrogen can be reoxidized to nitrogen-acids; but they escape with the other gas, and thus cause a loss of nitre.

We will now consider the opposite case, viz. that *the chambers receive too little steam*. According to the theory of the vitriol-chamber process, to be developed in the 9th Chapter, this must deteriorate the conditions for the formation of sulphuric acid, since the substance formed in an intermediate state, viz. nitroso-sulphuric acid, cannot then be entirely decomposed into sulphuric acid and nitrous acid. It will in this case be either separated in the solid state, as "chamber-crystals," or else it will dissolve in the bottom-acid. In actual practice it rarely happens that the deficiency of water is so great as to lead to the occurrence of solid chamber-crystals within the chambers; more frequently this happens in the connecting-pipes. But it is all the more general, nay unavoidable, that some chamber-crystals (commonly called "nitre" in this case) dissolve in the bottom-acid. We shall see later on that a certain quantity of "nitre" *must* be present in properly working chambers; but if there is too little steam, this

* Whenever here, and in other places, we speak of "steam" in connection with the supply of chambers, water in the shape of spray or mist is also meant. It would be tedious to mention this in every single case.

quantity will be largely increased, both by a deficiency of water in the acid mist floating about, which leaves a large quantity of nitroso-sulphuric acid undecomposed, and by the excessive concentration of the bottom-acid, which enables it to hold more "nitre" in solution. Thus the nitre will be removed from its proper sphere of action, the atmosphere of the chamber, and SO_2 will escape oxidation. Where the chamber-acid is directly used, without first passing it through the Glover tower, this nitre will be finally lost. All this, of course, happens less easily where the bottom-acid is kept at a lower strength, as on the Continent; there is in this case more time for repairing a temporary deficiency of steam as indicated by testing the drips and bottom-acids for strength and nitre.

A deficiency of steam also acts in this way, that the vitriol, becoming too concentrated, may to some extent act upon the lead. So long as the strength of the chamber-acid does not exceed 144°Tw . (and this will very rarely happen, even with faulty management), the harm is not much. For very good reasons, the last chamber, if a Gay-Lussac tower is present, receives very little steam, in the case of smaller chambers (tambours) none at all. But this may be carried too far; and then, in spite of the dark-red appearance of the chambers, there is a bad yield of vitriol, because the water necessary for its formation is missing, and SO_2 and O go away uncombined. This occurs especially when the chamber appears of a very clear, transparent red, instead of being somewhat dim and misty.

On the whole, it is evident that the risks run by a deficiency of steam are nothing like so serious as those arising from an excess of steam.

Hurter ('The Manufacture of Sulphuric Acid,' Liverpool, 1882, p. 16) gives the following rules for utilizing the indication of the chamber-drips:—

1st. If the strength of the acid in the drips is *correct* but deficient in quantity, the chamber is short of nitre.

2nd. If the strength is *high* and quantity not far short, the chamber is very rich in nitre; but if the quantity is short, it has too little steam.

3rd. If the strength is *low*, but the quantity full up, the chamber has too much steam. If, on the other hand, the strength is low and the quantity short, the chamber is very poor in nitre.

It is needless to say that the indications afforded by these rules would be sometimes very misleading, the conditions being too complicated, if they were not supplemented by direct observations of the amount of "nitre," the temperature, and the composition of the inlet- and outlet-gases, as shown below.

Supply of Nitre.

It is quite evident that those ingredients from which sulphuric acid is ultimately formed, namely sulphur dioxide, atmospheric oxygen, and water, must be supplied to the chambers in proportions varying within very narrow limits only, as any undue excess or deficiency of one of these will cause a corresponding waste. Sulphur dioxide being considered as the given quantity, the proportion of water supplied is kept so that a very nearly constant concentration of the chamber-acid is obtained; and in like manner the supply of air is regulated by the draught in such a way that a certain necessary excess of oxygen, but no more than this, is found in the exit-gas. But the matter is different with that reagent which does not enter into the composition of the ultimate product, and only serves as an intermedium for combining SO_2 , O , and H_2O , without (in theory) suffering any real change or loss at the end of the process. This is, of course, the "nitre," by which expression we understand all the compounds of nitrogen which are concerned in the manufacture of sulphuric acid, at whatever stage of oxidation or combination they may exist at a certain moment.

It is almost self-evident that the acid-making process can be made more or less rapid by supplying more or less nitre, and that this finds expression in the greater or smaller space which the process requires. In fact considerable variations may be made in the supply of nitre, according to whether the chamber-space is to be utilized as fully as possible or not, and up to a certain extent it may be said that the supply of nitre must change in an inverse proportion to the chamber-space present. But certain limits do exist here as well, both in an upper and in a lower direction. If there is too small a supply of nitre, the reactions become too sluggish and very disastrous consequences follow, which cannot be avoided by any amount of chamber-space; and if too much nitre is supplied, the temperature rises too much, the chamber-lead is acted upon, and part of the nitre escapes the process of recovery. We shall see this in detail hereafter.

The *supply of nitre* must be regulated on entirely different principles, according to whether there is an apparatus for the recovery of nitre or not. In the latter case care must be taken not to have too much nitre-gas in the last chamber; for every thing issuing from it is a total loss. Therefore the last chamber but one is kept strongly yellow or red, in order to advance the acid-forming process, but the last chamber only faintly yellow.

The bottom-acid in the latter, which is usually kept at 50° Tw., or even below, will partly absorb the nitre-gas as nitric acid, and there will not be so much of it lost. This state of the last chamber is attained by giving it much steam; but it will be seen at once that in this chamber very little work can be done unless a very large loss of nitre is suffered; for only if the latter be present in large quantity will the oxidation of sulphurous acid go on all through the chamber. Therefore one of these two things must be done: either a large quantity of nitre must be sacrificed in order to utilize the last chamber, or the last chamber is practically used only for recovering part of the nitre; thus actually a third or a fourth of the chamber-space is sacrificed, and so much less sulphur can be burnt in that set. For all that, the last chamber is not merely a costly but also a very inefficient apparatus for recovering the nitre; even if used as such, very little below 10 per cent., mostly above 10 per cent., of nitre to the sulphur must be employed in order to get a good yield. With poor, badly burning ores, of course, even more nitre is consumed, corresponding to the excess of air.

These considerations will make it evident how much more rational it is to *recover the nitre* by a proper apparatus. By this there is a saving of a fourth, up to a third, in chamber-space, at least one of two thirds in nitre, and mostly also better yield, because up to the last an excess of nitrous gas is present, and no sulphurous acid can escape oxidation by it. In this way any escape of noxious vapours is also much more completely prevented. The construction of the nitre-recovery apparatus, and every thing pertaining thereto, will be described in the next Chapter. Here we shall only describe the way of managing the chambers themselves in this case. Supposing the set to consist of three chambers (the reader will easily reduce this to any other proportion by analogy), the first chamber into which, in any case, both the gas from fresh nitric acid and that from the nitrous vitriol are introduced, whether it be by nitre-ovens, or cascades, or Glover towers, or steam-columns, will always

have an excess of nitre-gas. In spite of this the characteristic yellow and red colours of nitrous and hyponitric acids in the gaseous state will not be perceived in the first chamber, both because the sulphurous acid, likewise present in excess, constantly reduces most of the nitrous and hyponitric acids to colourless nitric oxide, and because the formation of sulphuric acid, principally going on in this chamber, generates in large quantities the well-known heavy white clouds. The whole atmosphere of the chamber is filled with these, and, owing to its opacity, its colour cannot be clearly recognized. In the second chamber the atmosphere is already much clearer; and as also there is very much less sulphurous acid present, a portion of the higher nitrogen oxides will be perceived by their peculiar colour. There is, however, still so much sulphurous acid present, that the mixture of gases in the second chamber will only show a more or less reddish yellow.

In the third chamber, however (in a set of more chambers, in the last—in a single chamber, in its last portion), the nitre-gas should largely predominate. There ought to be very little sulphurous acid here; and before the gas issues out of the chamber into the absorbing-tower, the sulphurous acid ought to be entirely removed from it. This is only possible by a large excess of nitrogen acids; and as, according to previous explanations, there is also oxygen present (5 to 6 per cent. by volume), that excess will not exist as colourless nitric oxide, but as red nitrous anhydride. This is proved by the last chamber showing a dark-red colour, sometimes so deep as to be opaque. Even in the much shallower layer of gas seen in the "sight" of the pipe leading to the absorbing-tower, the red or orange colour ought to be quite decided. Within the chamber the red ought to be not quite transparent, but dimmed by a mist of water (comp. p. 461).

The *colour of a chamber* can be observed by opening the man-lids on the top or the clay plugs in its side, but in a much more convenient and accurate way by glass windows put in the sides of the chamber itself (as described, p. 398). As soon as the last chamber gets paler, the cause of this must be sought for. It may be that it has got too much or too little steam or too little nitre; but it is always a sign that something is wrong; and by comparing the other symptoms, especially the strength and the nitrosity of the drips and bottom-acids, the special cause of the fault must be got at. When the last chamber becomes quite pale, it is certain

that a great loss is suffered by sulphurous acid escaping from it; and the latter, on its way through the Gay-Lussac tower, will even denitrate the nitrous vitriol contained therein, and cause a loss of nitre in the shape of nitric oxide escaping into the outer air. Every thing must therefore be done to avert the above phenomenon.

Apart from the colour, the gradual diminution of sulphurous acid and increase of nitrogen acids in the chamber-gas as it proceeds on its way can be perceived from other signs, such as the *smell* and the *chemical analysis* of the gas. The judgment by smell is so much more uncertain and inexact than that by colour that it is not worth while to enter upon it in detail. A chemical analysis of the gas would certainly permit the reaction in the individual chambers to be traced with ease and safety; but this plan is not usual, and even the best continental works only make two gas-analyses—that of the burner-gas before entering the chambers, and that of the gas finally leaving the apparatus as it issues from the Gay-Lussac tower. It would give some little trouble to analyze the chamber-gas between as well; nor is this necessary, since its colour gives a sufficient indication for the purpose in question.

Along with testing the *chamber-acid* for its strength, it is of great importance to test it also for its *nitrosity* (percentage of nitrogen acids); and this forms a necessary complement to the observation of the colour of the chambers. Under normal circumstances the percentages of nitrous acid (or rather of nitrosyl sulphate) and of nitric acid in the chamber-acid are so small that its quantitative estimation by the usual method is very inaccurate, especially because a number of impurities interfere with the accuracy of the process. In practice, however, a simple and momentarily made colorimetric test with ferrous sulphate is sufficient for the object in question.

When a solution of ferrous sulphate is poured upon the drip- or chamber-acid contained in a test-tube so that the liquids are not mixed, a yellow ring is formed at the point of contact, if traces of the higher nitrogen oxides are present. With more nitrogen oxides the ring becomes darker; with still more the whole ferrous sulphate solution assumes a deep brown or black colour. In this case effervescence readily sets in, the liquid getting hot, and the dissolved nitric oxide, with the black colour,

being driven off by the heat. With some practice, and always working exactly in the same way, it is quite possible to get a good idea of the percentage of nitre in the chamber-acid by its appearance under the above conditions. The testing for a set of four chambers can be carried out in this way:—A stand containing eight ordinary test-tubes of 5 inches height is once or, preferably, twice a day taken to the chambers, and the tubes filled up to about 4 inches with samples of the drip- and bottom-acids of each chamber; at the same time the strength of each sample is taken by the hydrometer, and written on the stand at the bottom of each tube. The acid-samples are then tested, at any convenient place, by carefully pouring on to each about a half inch of a concentrated solution of ferrous sulphate, which need not necessarily be free from ferric sulphate. By looking at the colours produced thereby, in their succession from chamber to chamber, by comparing the drips and bottom-acids, looking at the strengths marked below, and taking into account the colour of the chamber-gas observed through the windows, a tolerably good idea of the process going on in the chambers is obtained. This certainly should be completed by an estimation of the sulphurous acid in the burner-gas and of oxygen in the escape-gas, and also by testing the nitrous vitriol &c., as we shall see in the next Chapter.

Kolb (Bull. Soc. Mulh. 1872, p. 309) gives a few analyses of chamber-acids confirming what has just been said.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>	<i>f.</i>	<i>g.</i>	<i>h.</i>
Density	1·489	1·417	1·445	1·480	1·488	1·478	1·420	1·457
SO ₄ H ₂	59·1	51·6	54·9	58·1	58·6	58·2	51·4	56·0
N ₂ O ₃	0·023	...	0·04	0·023	0·010	0·02	0·170	0·03
N ₂ O ₅	0·000	...	0·02	0·000	0·000	trace	0·040	0·00
SO ₂	0·008						

a, acid from the first or denitrating tambour, where the sulphurous acid of the burner-gas meets the acid of the last chamber and the Gay-Lussac tower; *b*, the same when the chambers were short

of nitre; *c*, acid from the tambour where the fresh nitric acid ran over the "cascade" (excess of nitre); *d*, the same, short of nitre; *e*, acid of the "large chamber;" *f*, acid of the last chamber, normal process; *g*, the same, large excess of nitric acid—liquid green and nitrous; *h*, the same, normal process.

The following rules may be laid down for the reactions which the various samples of acid from the chambers and drips ought to show. Generally speaking, all drips ought to show more nitre than the corresponding chamber-acids. The former represent the process going on in the atmosphere of the chamber, whilst the latter should act upon the nitre by their greater dilution, and actually do so. The *bottom-acid* of the *first or leading chamber* ought not to show any nitre whatever; if it does so, it is a strong indication that the supply may be shortened. (It must be borne in mind that a slight quantity of nitre, which can be discovered by finer tests, is nearly always present even in the first-chamber acid, but the described rough test ought to show none or next to none.) But first it must be ascertained if, on the other hand, the drip of this chamber does not show any nitre; for in this case it is proved that there is *too little steam* in the chamber, and that consequently the nitrous acid has been absorbed by the chamber-acid. Mostly this will be confirmed by both drip and bottom-acid being too strong; and then *more steam* must be given. If, however, *both* samples from the first chamber show nitre, some of the latter must be cut off, unless the supply has just been increased because the last chambers did not show enough; in this case the supply of nitre cannot be cut down till the last chambers have quite recovered.

Sometimes the first chamber-acid smells, on the contrary, of sulphurous acid: if this is the case to any appreciable extent, nitre is wanting.

The *middle* chambers ought to show already a faint reaction of nitre in the bottom-acid, and a stronger one in the drips; the *last*, in any case, a moderately strong reaction in the bottom-acid and a very strong one in the drips. In this case also a deviation from the rule may proceed from various causes. For instance, the last chamber may be pale, and yet its bottom-acid may give a strong nitre-reaction. This may happen both if there is too much and if there is too little steam in this chamber: if the bottom-acid is too strong owing to the want of steam, it will dissolve too much nitre;

if, however, there is too much steam present, that phenomenon will take place which, in chambers working without an absorbing-tower, is purposely caused: nitric acid will be formed, and will dissolve in the bottom-acid. Both faults are easily avoided if the last chamber is not kept weaker than 90° nor stronger than 110° Tw.; but sometimes insufficient draught may cause that fault as well. If, on the contrary, the last chamber still appears red, and even the drips still show nitre, but the bottom-acid none, this is an indication which must be instantly met by increasing the supply of nitre; otherwise the chamber itself will soon become pale. If both indications coincide, a pale chamber and a ceasing or weakening of the nitre in the drip, this might still come from an excess of steam; but rarely will it be so, as anyhow that chamber does not get much steam. Three other explanations offer themselves—too little draught, too much draught, or too little nitre. Whether the draught is insufficient is most easily tested by estimating the oxygen in the escape-gas; whether it is too large, by estimating the sulphurous acid in the burner-gas; but in the case of very leaky chambers, which properly ought to have been stopped already, air enters directly into them, as is proved by the oxygen coming out too high in the escape-gas. Where no gas-analyses are made, the formerly mentioned external indications for judging of the draught are taken into account; but these are far more deceptive than gas-analyses. When the draught is not large enough, the nitric oxide does not meet enough oxygen to be oxidized; it is colourless, and, owing to its insolubility in strong vitriol, is altogether lost. This will be recognized by the appearance of red vapours on the gas issuing out of the chimney, where the nitric oxide is oxidized by the atmospheric oxygen, whilst the chambers themselves, where oxygen is missing, become pale. When there is too much air present, the nitrogen acids are carried away mechanically, and the chambers equally lose their colour; at the same time sulphurous acid goes away, as it has not time to be oxidized.

Insufficient formation of sulphuric acid in the chambers, from other causes, such as want of nitre or entering of air through chinks in the chambers and mechanical carrying-away of gas, will frequently *react upon the burners*, since by the insufficient condensation of gas the draught from the burners towards the chambers is diminished. Then all the appearances will take place which

are caused by very bad draught in the burners, especially incomplete burning and formation of scars, which, again, weakens the draught. In this case as much nitre as possible must be given, in order to force a better formation of sulphuric acid; and, if necessary, even the burner-charges must be diminished.

But if the last chamber becomes pale, the draught being in order, and if its acid shows little nitre, it is just the want of the latter, and more of it must be introduced till the normal state has been restored. This will be confirmed by *testing the nitrous vitriol*, which will no doubt show a diminution of its nitre. Undoubtedly several circumstances often act at the same time, and make the process a complicated one. If, for instance, there is too little draught, so that, in lieu of N_2O_3 , only NO or even SO_2 get into the absorbing-tower, not only will the draught have to be increased, but more nitre will have to be given as well, in order to make up for the loss. Just in the same way, when the nitre-gas has been mechanically carried away by an excess of draught (in which case, owing to its dilution, the Gay-Lussac tower cannot entirely retain it), not only will the draught have to be moderated, but more nitre will have to be introduced till every thing is in order again.

An *excess of nitre* is detected by the colour of the chambers being too dark, by the strong nitrosity of the acids, and by the fact of the Gay-Lussac acid showing the presence of nitric acid, consequent upon the formation of N_2O_4 in the last chamber, which is irregular (see Chap. VIII.).

We thus see that, in nearly every case, when any thing goes wrong in the acid-chambers, an increased supply of nitre is at least temporarily necessary in order to restore the equilibrium, although the other two regulators, steam and draught, must always be taken into account at the same time; it is therefore very important that the possibility be afforded of temporarily introducing much more nitre into the chambers than is necessary in ordinary work; and every factory ought to possess facilities for it. If this should not be the case to a sufficient extent, and if without danger to the chambers it is not possible to introduce as much nitre as the case calls for, then nothing remains but to diminish the burning of brimstone or pyrites for a time, and to allow the chambers to recover their normal state by easing them in this way.

A proposal made by the Manufacture de Javel (E. P. 1752, of 1882) seems to be worthy of more notice than it has received. The nitre

is not to be introduced into the leading chamber only, where the temperature may thereby become exorbitantly high, but to a small extent also into the following chambers, whose temperature is sometimes too low. Even the acid for feeding the Gay-Lussac tower is to contain a little nitre, in which case no SO_2 can escape through the tower.

A similar proposal is that of the United States Chemical Company, Camden, N.Y. (Am. P. 325, 262, of 1885), to inject nitrous vapours into the last chamber eventually, after having first injected steam, in order to counteract any too strong reduction of the nitrogen-oxides.

At some of the best-conducted works it is not thought sufficient to judge of the supply of nitre by the colour of the chambers, the testing of the drips, and so forth, but a system is introduced of constantly checking the amount of nitrous vitriol supplied to the Glover towers, its strength, and the amount of fresh nitre or nitric acid introduced in comparison with the amount of sulphur burnt, in order to keep the quantity of nitre present in the chambers at as constant a figure as possible. As an example of the way in which this account can be kept, I give the following figures, taken from an actual day's work in a well-conducted continental factory:—

	Set No. I.	Set No. II.
Pyrites burnt, kil.	10812	10000
Containing sulphur, less quantity left in cinders	4993	4735
Nitrous vitriol used, kil.	10138	10268
Average strength, expressed in nitric acid 36° B.....	4.86	4.37
Equivalent to acid of 36° B., kil.	493	449
Fresh nitric acid supplied, kil.....	200	186
Total as nitric acid 36° B., kil.....	693	635
Equivalent to 96% nitrate of soda, kil. ...	520	476
96% nitrate introduced for each 100 parts of sulphur burnt	10.4	10.1

This quantity, about 10 parts of 96% nitrate to 100 of sulphur, may be considered a minimum, and only admissible where the chamber-space is very ample—say, about 24 cub. ft. per lb. of sulphur. With less chamber-space, much more nitre, equivalent

to 15 or even 20 parts of 96% nitrate of soda to 100 sulphur burnt per diem, is put through the system. For the "forced" style in France up to 25 parts of nitre is used; but this involves a correspondingly large nitre-recovery apparatus, without which the waste of nitre would be very serious.

Pemberton (J. Soc. Chem. Ind. 1883, p. 414) quotes a total supply of 15.6 parts of nitre passing through the chambers for every 100 parts of sulphur burnt in the shape of brimstone, with 19.2 cubic feet per lb. of sulphur. In this case a Gay-Lussac tower was used; whilst in three other cases, where there was no Gay-Lussac, from 8 to 10 parts of nitre was consumed, but with 26.8 to 35.7 cubic feet of chamber-space. As he gives no details as to yields, his figures possess very little value.

Temperature.

At every sulphuric-acid works the *temperature of the chambers* is a subject of constant observation on the part of the attendants, and it is generally understood that the regular and economical working of the process is intimately connected with keeping the temperature at a certain height, different in different parts of the same set of apparatus, and considerably varying in analogous parts of the apparatus at different works, but to be kept as nearly as possible equal and constant in the same place. The care with which the observations of temperature are made certainly varies very much. In Germany for many years past thermometers have been fixed in several places of the chambers, generally near the "drips" (p. 395), and their readings are regularly recorded. In France and particularly in England this has been very much less the case; even in large and otherwise very well-managed works chamber-thermometers are frequently not to be found, and it is thought sufficient to test the temperature of the chambers by putting the hand upon the lead. It is hardly necessary to say that the latter plan is decidedly faulty, and the small expense and trouble of applying and using thermometers ought never to be shunned.

This is independent of the question, whether a certain temperature is or is not the theoretically best for the process of sulphuric-acid making, and whether this is the *cause*, or the *effect*, of the economical working of the chambers; for there is no diversity of opinion as to the fact that all causes leading to a faulty process

act either directly or indirectly on the temperature of the chambers, and that the observation of the latter is one of the most important guides for judging of the proper working of the acid-making process.

Considerable diversity of opinion exists concerning the best temperature for the chamber-process; but there is no doubt as regards some general facts. The temperature of each chamber diminishes from front to back, and naturally even more that of the last chambers compared with the first. All these differences in the normal process ought to be constant. The first chamber will be generally so hot that one cannot touch it for any length of time, say 50° to 65° C.: in the absence of any cooling-apparatus, Glover tower, &c., the heat becomes so high that the lead cannot be touched with impunity; but in that case the chamber will not last very long. The second chamber mostly shows on the outside hardly more than blood-heat; thermometers with their mercury-vessels inside the chambers show from 40° to 60° C. The third chamber, if it be the last, will outwardly show little or no difference in temperature from the surrounding atmosphere; inside its temperature varies from 40° to 30° , and below that.

At the Aussig works in September the tambour showed 60° , the large chamber in its first part 45° , in its last part 43° ; the first back chamber 30° , the last (kept without any steam) 20° C. At Oker the leading chambers in winter vary from 60° to 69° ; the large chamber in its first part from 25° to 31° , in its last part from 19° to 25° ; the back chambers 0° to 10° C. In summer the average temperature is $12\frac{1}{2}^{\circ}$ C. higher than in winter.

At Salindres the leading chamber is kept at an average of 65° in summer, of 55° in winter. This is a refutation to the assertion of Favre (*Monit. scient.* 1876, p. 272), according to whom in the south of France the chamber-process is already disturbed at 65° . But it is true that many skilled chamber-managers prefer working the leading chamber as nearly as possible at 50° to 60° only.

Dr. Stahl informs me that in a set of three chambers for brimstone, working without a Glover tower, but where part of the heat of the burner-gas was employed for concentrating acid, as shown *suprà*, p. 196, the temperature ranged as follows:—

In the first chamber, near the entrance of the gas, from 80° to 90° C., according to the outside temperature.

In the second (main) chamber in the middle from 50° to 60° C.

In the third chamber about 10° C. above the outside temperature in summer, and 20° C. in winter.

The opinion expressed by H. A. Smith, according to whom the best temperature would be nearer 100° , is not based on any valid reasons, and seems to be shared by very few practical men; on the contrary, such high temperatures are universally assumed to be extremely injurious to the chamber-lead and are carefully avoided. In Europe 90° or 95° is probably the maximum temperature found anywhere; but in America I found in one place, where zinc-blende was burned, a temperature of 110° , and it was asserted that this chamber (of course, the first of the series) suffered less than the last; but they had only a few years' experience at that works, so that we cannot accept the statement as conclusive.

The *lower* limit of temperature is by Schwarzenberg put at 40° to 50° C., because otherwise there would not be a sufficient quantity of water remaining in the state of vapour; he asserts that in cool weather a set of chambers is less easily started than in warm weather, and that in winter more nitre is used than in summer. I must contradict this assertion of Schwarzenberg's, both from his own and from many other practical men's experience. Unless the temperature of the chambers sinks so low that ice is formed in them (which may happen with back chambers kept without steam), no excess of nitre is required in winter; on the contrary, at all well managed factories known to me it is asserted that they regularly require less nitre in winter than in summer, and that the work altogether proceeds better in the cooler season.

We have also seen (p. 422) that it is a mistake to assume that the water exists principally in the state of vapour within the chambers.

A most remarkable case is presented at the Freiberg works, where the cooling of the burner-gas, in order to condense the arsenious acid, is carried on so far that the temperature is that of the outer air, and in winter the gases often enter the chambers at 0° . In spite of this, no inconvenience is felt, and no special contrivances or precautions need be employed; the temperature within the first chamber soon rises to 60° and upwards.

On the other hand, it cannot be doubted that there is at all events an upper limit, beyond which the temperature of the chamber ought not to go. We have seen in Chapter III. (p. 159) that with the same gaseous mixture a comparative slight rise of temperature, from 70°

to 80° , is sufficient to convert the oxidation of NO to N_2O_3 into a reduction of N_2O_3 to NO. Unfortunately we do not yet know the conditions of the process to the extent necessary for *à priori* fixing the upper limit of the temperature of the chambers with any approach to certainty.

In normal circumstances the temperature of the first (leading) chamber will have a direct relation to the quantity of work put upon the system. Whilst with the ordinary allowance of 20 cubic feet per lb. of sulphur the normal temperature is, as before said, from 50° to 60° , or at most 65° , it is, with forced work (15 or 12 cubic feet per lb. of sulphur), 80° at the inlet and rises to 90° or 95° further on; even at the outlet it is still 15° or 20° over the temperature of the ambient air.

The temperature of the chambers depends upon various causes. It is raised by the heat of the burner-gases, by that of the steam introduced, and (in a far greater ratio) by the chemical reactions of the acid-making process; sometimes, in warm countries and in unprotected chambers, by the heat of the sun. Part of this heat is withdrawn by the radiation from the thin and quickly-conducting leaden walls of the chamber, also by the heat contained in the escaping gas and in the acid drawn off. The loss of heat by radiation will vary according to the season, to the wind, &c., but, of course, much less with chambers inclosed in buildings than with those exposed to the weather. As for a given time both this influence and the heat brought in by the burner-gases and withdrawn by the exit-gases and the acid manufactured vary but little. the inner temperature will practically be ruled by the intensity of the chemical reactions.

The facts now stated prove by themselves that, as I have urged before, *frequent observations of the temperature of the chambers are of great importance for the proper management of the process.* Although the temperatures at the various parts of the apparatus show very great discrepancies at different works, they are almost constant in the same set of chambers, as long as everything is in good working order; and for this reason any considerable rise or fall of the thermometer, to the extent of say 5° C., is a certain sign that there is some irregularity which should be remedied. This indication is all the more valuable as it is instantly observed without requiring any tests or loss of time, and it is accessible to any ordinary working-man without the aid of a chemist.

One of the most systematic observations of the temperatures in different places of a set of chambers was made at the Uetikon works by Lunge and Naef (Chem. Ind. 1884, p. 17). Three readings were made every day, and the following are the averages of a prolonged period, both for (A) Moderate duty of chambers (4.4 tons pyrites for 129,000 cubic feet, or 29 cubic feet per lb. of sulphur), and for (B) Intense duty of chambers (6 tons pyrites, or 20.8 cubic feet per lb. of sulphur). The strength of the acid in the "drips" fixed near the thermometers is also indicated. The extreme variations of the chamber-temperatures, of which only the averages are given here, did not exceed 3° or 4° C. The temperature of the outer air varied far more, viz., 3° to 17° in the 14 days' working of A, and from 5° to 20° C. in the 10 days' working of B; but this did not influence anything except the last chamber. The chambers had all the same width (28 ft. 4 in.) and height (23 ft.); but the leading chamber was 138 feet, the second 65½ feet, and the third 36 feet long.

	A. Moderate duty.		B. Intense duty.	
	Temp. ° C.	Strength ° Tw.	Temp. ° C.	Strength ° Tw.
Pipe coming from Glover tower	65	—	75	—
Front of leading chamber, near bottom ...	60	123	69	123
Middle " " near bottom ...	60	112½	71	116
" " " midway up	61.8	—	73	—
" " " near top	64.5	116	76	116
Pipe between first and second chamber.....	45	119½	57	—
Second chamber near bottom	32	116	41	116
Pipe between second and third chamber ...	27	—	35	119½
Third chamber	19	116	24	116
Outer air	9	—	12	—

This shows in the first chambers a difference of from 9° to 12° between moderate and intense duty of the chambers. The temperature was very distinctly influenced by the quantity of nitre: with strongly red chambers it was much higher in the front than in the back part; with paler chambers the difference was less, the reaction also going on more equally. At the top of the first chamber the gases were from 4° to 5° hotter than at the bottom, but gas analysis showed that the gases were not richer in SO₂ and O in the former than in the latter case.

Further experiments were made on the cooling-influence of the radiation from the chamber-walls. The following are the average of seven days' observations at distances of 10, 4, and 2 inches from the chamber-side, with an average outer temperature of 19° :—

	Distance from chamber-side.		
	10 in.	4 in.	2 in.
Pipe from Glover tower	78	71	68
Front of leading chamber	72	71	68
Middle " " near bottom.....	74	73	70
" " " midway up	76	75	73
" " " near top	80	79	77
Second chamber	52	51	50
Third chamber	33	33	33

At an outer temperature of 19° , therefore, the cooling between 2 and 4 inches from the chamber-side averaged only 2° , between 4 and 10 inches only 1° . At lower outside temperatures of course the cooling action would be somewhat stronger. Greater differences were found when the following observations were made in the centre of the chamber by lowering a maximum thermometer by means of a wire through the chamber-top and reading off at the other places as before (the table gives the average of 10 observations, at an average outside temperature of 18°) :—

Pipe from the Glover tower	73 ^c
Front of leading chamber	69
Middle of ditto, 10 inches from side, bottom.....	70
" " " " midway up	72
" " " " top	76
" " " " centre of chamber, bottom.....	75
" " " " midway up	78
" " " " top	80
Second chamber	50
Third chamber	29

This shows a difference of 5° between the centre and a place 10 inches from the sides, so that there would be 8° between the centre and the sides. This would seem to show that the hot current moves less quickly in the centre than near the sides, and it agrees with the fact that the percentage of SO_2 and O in the centre

is greater, that is, that the reaction is less advanced there than near the sides in the same transverse section of the chamber. This would agree both with the theory of Abraham (to be mentioned further on), according to which the gases move in a spiral course from the front to the back end of the chamber, and with that of Sorel, as we shall see in Chapter IX.

The preceding observations clearly show that the chemical reactions produce a rise of the temperatures, as the heat of the gases in the middle of the leading chamber near the top exceeds even that of the gases arriving in the Glover tower, in spite of the cooling action of the air traversing a distance of 70 feet from the front to the place of observation. This is confirmed by special observations in the fore part of the chamber, where the formation of acid is most vivid:—

	Bottom.	Midway.	Top.
33 feet from front end ...	80·5°	83°	81°
66 " " " " ...	75	78	80

Special interest is also afforded by observations made to find out the effect of using either *steam* or a *spray of liquid water* for feeding the chambers.

	Steam. (Outer temp. 12°.) °C.	Water-spray. (Outer temp. 24°.) °C.
Pipe from Glover tower	69	73
Leading chamber, bottom	71	73
" " midway	73	75
" " top	76	78
Pipe from first to second chamber	57	68
Second chamber	41	53
Pipe from second to third chamber	36	47
Third chamber	24	31

It is true that in the second case (water-spray) the outer temperature was 12° higher than when using steam; but we have seen above that this influences especially the first chambers but little, and we may thence conclude that there is no sensible difference in temperature between the application of water as steam or that as liquid spray. All this confirms the paramount influence of the chemical reactions.

The following diagrams, figs. 178 to 182, show the just-men-

tioned results graphically, the length of the chambers being approximately represented. In fig. 178 the thick line represents the temperature-curve for a normal duty (20·8 cubic feet chamber-

Fig. 178.

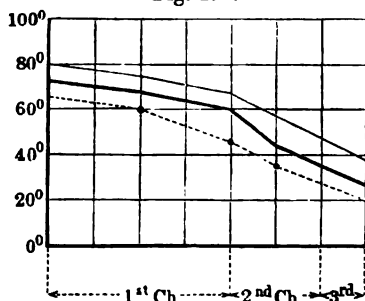


Fig. 179.

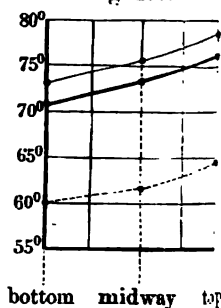


Fig. 180.

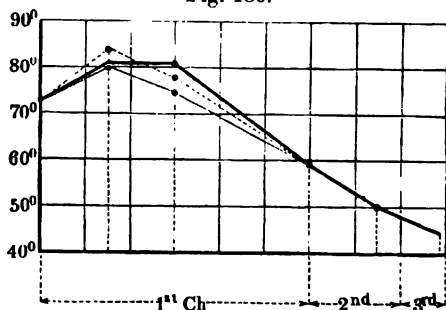


Fig. 181.

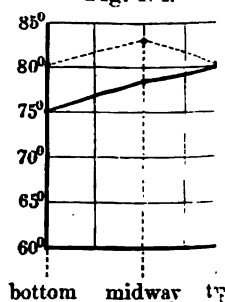
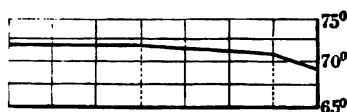


Fig. 182.



space), at 12° C. outer temperature; the dotted line for moderate duty (29 cubic feet), at 9° C. outside; the upper faint line the temperatures observed with a liquid water-spray at 24° outside. Fig. 179 gives the temperatures, obtained in the same series of experiments, as observed in the same transverse section near the bottom, midway, and near the top (the lines have the same meaning as in the preceding figure). Fig. 180 shows the temperature-curves in the longitudinal section of the chambers; the dotted line representing the observations taken at midway height, thin line the bottom, and the thick line the top. They show very

clearly how the temperature is raised by the chemical reactions; near the bottom and at a midway height it begins to fall in the second quarter of the leading chamber, but at the top it keeps up as far as midway. Fig. 181 shows the temperature at different heights in the centre of the first chamber; the thin line at a distance of 33 feet, the thick line at 66 feet from the front end. Fig. 182 shows the increase of temperature from the outside towards the inside (cooling action of the walls).

Eschellmann (J. Soc. Chem. Ind. 1884, p. 135) has proved numerically the relative importance of steam and nitre in the temperature of the chambers.

Taking the drips in the first chamber = 130° Tw., this corresponds to the compound $\text{H}_2\text{SO}_4, 2 \text{H}_2\text{O}$ (molecule = 134), or to an evolution of $53,480 + 9,418 = 62,898$ calories for 134 grammes of that acid. The 54 grammes of steam, at 125° C., required for forming $\text{H}_2\text{SO}_4, 2 \text{H}_2\text{O}$, represent 34,809 calories. We will now assume that more steam is introduced, and we will put an extreme case, viz., the formation of $\text{H}_2\text{SO}_4, 3 \text{H}_2\text{O}$. This means another 18 grammes steam at $125^{\circ} = 11,603$; whilst by the reaction $\text{H}_2\text{SO}_4, 2 \text{H}_2\text{O} + \text{H}_2\text{O}$, 1,729 calories are evolved. We must, however, deduct the heat corresponding to a chamber-temperature of $50^{\circ} = 50 \cdot 087$ calories per gramme of water, which is left in the product, and we thus arrive at the following figures:—

The formation of:

$\text{H}_2\text{SO}_4, 2 \text{H}_2\text{O}$ evolves $62,898 + 32,105 = 95,003$ cal.

$\text{H}_2\text{SO}_4, 3 \text{H}_2\text{O}$ „ $95,003 + 10,702 + 1,729 = 107,434$ cal.

Taking the gas entering the chambers to contain 6 vols. SO_2 in 100, this means introducing in the first case 3×6 vols. H_2O , and increasing the total to 118 vols.; in the second case 4×6 vols. of water, or a total of 124 vols. Thus we have—

For 118 vols. an evolution of 95,003 cal.; 1 vol. = 805.

„ 124 „ „ 107,434 „ ; 1 „ = 867.

Now taking the chamber-temperature at 50° , the outer air at 15° , the difference of 35° must be produced by the above reactions. The proportion $805 : 867 :: 35 : 37 \cdot 6$ shows us that introducing so much more steam that the quantity of water in the sulphuric acid is increased by a whole molecule (and thus bringing down the drips from 130° to 110° Twaddell) makes a difference of only $2^{\circ} \cdot 6$ C. in the chamber-temperature. The maximum variation

produced by changes of the outside temperature, even in summer, when they are greatest, were not found to exceed 5° C. On the other hand, the following observations were made concerning the influence of the *nitre* on the chamber-temperature. Two sets of chambers, burning about equal quantities of pyrites, were supplied with their nitre exclusively by means of nitrous acid from Gay-Lussac towers, and therefore in a continuous fashion, while all the potting of fresh nitre was done in a third, larger, set of chambers, at intervals of two hours. Now the two small sets show no variation of temperature except what is due to the variation of the surrounding air, namely, between 50° and 53° C., but the large set shows a regular variation from 48° to 68° C., the lowest temperature occurring immediately before potting, when the first chamber is least supplied with nitre, and slowly rising after the potting of fresh nitre. The thermometers were inserted at a distance of 22 feet from the gas-inlets; the temperature of the gas entering was 35° C. The difference between the small, continuously supplied sets, and the large, intermittently supplied set, as far as temperature is concerned, cannot be ascribed to any other cause than the continuous or intermittent supply of nitre. This was conclusively proved by a special experiment in which one potting was missed, so that the only supply of nitre to that set came from a small quantity of nitrous vitriol running down the Glover tower, amounting to but 20 per cent. of the regular supply. In this case the temperature of the gases, entering at 35° , rose only to 41° , the strength of acid at the drips fell rapidly, a large escape of sulphurous acid took place at the Gay-Lussac tower, and the chambers worked very irregularly, until not only the missed nitre was put in, but an additional quantity required to compensate for the nitre lost by reduction to nitrous oxide. Eschellmann's experiments are a strong argument in favour of the continental plan of feeding the chambers with nitric acid.

Sorel (Zeitschr. f. angew. Chem. 1889, p. 271) finds that the difference of temperature between the front and back end of the first chamber, measured 5 feet above the bottom, is only 2° , which is accounted for by the fact that the heat produced by the chemical reactions is only slowly abstracted from the gases by radiation from the walls. The space close to the lead walls is, of course, coolest (comp. p. 479); from here towards the interior of the chamber the temperature increases quickly, and in many

cases reaches a maximum at a distance of from 4 to 6 inches from the wall; after this it first sinks and then generally rises again towards the centre. Unfortunately, not many observations were made; but we will quote that series which is fullest (the temperatures, as remarked by Sorel himself, were extremely high, the season being very hot) :—

Close to the lead.....	78°·5 to 79°·7
At 2 centimetres distance.....	84
„ 4 „ „	91
„ 6 „ „	95·25
„ 8 „ „	95·25
„ 10 „ „	98·3
„ 12 „ „	97·3

Sorel believes that this difference of temperature is strong evidence in favour of Abraham's theory of the path taken by the gases within the chamber (see below); he also makes a most important use of it in his own theory of the formation of sulphuric acid (Chap. IX.).

We must also mention an abnormal state of matters which is sometimes observed, namely, a rapid sinking of the temperature of the first chamber, whilst that of the last chamber rises far above the proper degree. This is always accompanied by the colour of the gases getting paler, first in front, then also behind, so that even the last chamber may become quite grey. At the same time there is a great deal of liquid condensing on the glass of the "sights." Ultimately the quantity of sulphurous acid going away unoxidized may become so large that the nitrous vitriol within the Gay-Lussac tower is denitrated, and the nitric oxide escaping, on contact with the air outside, forms dense red clouds. This state of things is brought about by all the causes which disturb the proper process—want of water, want or excess of steam or of air: all of these tend to keep the process back, so that the first chamber does too little, and the last chamber too much work. An examination of the composition of the gases at the inlet and at the outlet, as well as of the strength and nitrosity of the drips, will lead to localizing the cause of the disaster and admit of applying the proper remedy. Usually, together with all other remedies, a fresh dose of nitre must be given, in order to get up

the temperature of the first, and reduce that of the last chamber; that is, to bring back the maximum of production to its proper place in front of the apparatus. Where it is impossible to get enough fresh nitre into the chambers, the pyrites-burners must be kept back, to diminish the amount of sulphide dioxide in the chamber atmosphere. At all events, the indications of the thermometer in the *last* chamber are very important; if it rises above the normal point, the proportion of sulphur dioxide to that of the nitrous gases and steam is sure to be wrong, and should be remedied at once before more mischief is done.

Depth of Acid.

It is a general belief among practical men in England that the *depth of acid at the bottom of the chamber* influences the completeness and regularity of the chamber-process. In their opinion the best yield and the most regular work is only obtained by keeping a good stock of acid in the chambers, say nine inches or more. I have myself, when in actual practice, shared that belief, without being able to adduce any positive proofs for it. On the contrary, a very experienced acid-maker, M. Delplace, decidedly denies that the process is improved by a great depth of acid. He was in a position to start a chamber (whose sides were burnt to the bottom) without any acid at all: the drops could be heard to splash upon the lead as they fell down; yet both the yield of acid and the consumption of nitre (1 part to 100 rectified O.V. were as favourable as in any other case. It must not be overlooked that a very great depth of acid diminishes the available chamber-space.

Concluding Remarks.

In checking the process it must never be overlooked that the same symptom may be owing to various causes. Thus the acid may get weaker either by a falling-off in the make or by too much steam. The draught may be lowered either by a smaller make, or by atmospheric influences, or by the gas-flues getting stopped up with deposit. An insufficient conversion of sulphurous into sulphuric acid may be caused by too weak or too strong a draught. The nitre may decrease in the chamber both from an excess of

steam, which leads to formation of nitric acid, and from a deficiency of it, leading to chamber-crystals getting dissolved in the bottom-acid; and in both cases the strength of the vitriol falls off. From the fact that in acid-making a certain effect may be caused by different circumstances, the management of chambers is not an easy task, but requires a good deal of judgment and experience.

Distribution of Gases and Rate of Formation in the various parts of the Vitriol-Chambers.

The following observations and considerations possess far more than a merely theoretical interest. They are intimately connected with the questions—which is the best shape for vitriol-chambers? are contact-surfaces for the better condensation of the acid to be provided, in addition to mere chamber-space? what is the real duty performed by the various parts of a set of vitriol-chambers, and can that duty be performed in a more advantageous way? and so forth. These questions have had to be treated to a considerable extent in preceding chapters (pp. 364, 365, 366, 369, 374, *et seq.*), and they will also influence the theory of the Sulphuric Acid Manufacture (Chap. IX.).

The experiments made by H. A. Smith, and recorded in his pamphlet, “On the Chemistry of the Sulphuric Acid Manufacture” (London, 1873; comp. *suprà*, p. 364), are entirely untrustworthy, as pointed out several times before, in more detail, in the first edition of this work, p. 285 *et seq.* His conclusion, that the chief portion of the acid made in the chambers is produced and condensed close to the surface of the acid already formed in the chambers, has not been confirmed by any other observer, and we will not detain ourselves any further with it, as it is also in direct contradiction to his own analyses of the gases. Hasenclever (A. W. Hofmann’s Report on the Vienna Exhibition, vol. i. p. 178) fixed lead dishes in several parts of his chambers, covering them over at a distance of a foot, and thus found that about the same quantity of acid was formed all over the chamber. [This conclusion certainly cannot be proved definitely in this way, as the dishes act as contact-surfaces; see pp. 376 and 484.]

Mactear (J. Soc. Chem. Ind. 1884, p. 224) has published an

extensive series of observations on the distribution and condensation of the gases in the vitriol-chambers. So far as they go towards settling the point at which part of the chamber the principal formation of the acid takes place, they are of no use to us, as they were based on a wrong principle, viz. that of observing the quantity of acid condensed on trays of a certain surface. It has been frequently shown, and that by Mactear himself in the same paper, that solid (or liquid) surfaces within the chambers have an intense condensing action upon the acid, which means that the mist of impalpably small drops on striking such surfaces condenses into large drops and collects upon the trays; hence the quantity of acid running away from the trays is not that made in the space above them, but represents a very much larger quantity, made partly, and possibly to the greatest extent, at some distance from the place where the tray is located.

How unreliable is the plan of testing the amount of sulphuric acid formed in a special part of the chamber by means of collecting-trays has been very clearly shown by Naef (*Chem. Ind.* 1885, p. 287). The condition supposed to exist by previous observers is this, that the trays collect all the acid formed in the vertical space above them. If it were so, next to no acid would be found when the tray is provided with a cover. If, however, the drops fall down in a slanting direction, some acid will be found, and its quantity ought to vary in proportion to the distance between the tray and the cover. But even this is not the case. Naef placed within the chamber on one side an open tray, and on the other side a tray with a wider cover, suspended over it at a variable distance. The result of weekly averages was this:—that the tray with the cover 12 inches above it collected exactly as much as the open one, and even when the cover was only 4 inches above the tray the acid collected was nearly as much as on the open tray. Repeated observations confirmed this result entirely. This surprising phenomenon cannot be explained by a slanting fall of the drops, for it would suppose the fall to take place at an angle of 20° , which cannot be produced even by the most violent movement within the chamber, far above anything which really exists. There is no other explanation than one to which a very large number of former observations in all possible cases, also those of Mactear, irresistibly lead—that the sulphuric acid, when formed, exists in the shape of a very fine mist which

is very slowly deposited in the form of a rain of real drops, and is carried forward by the gases for long distances, but is suddenly condensed to real drops when striking against solid [or, perhaps, liquid] surfaces. Therefore the acid is not at all deposited in a liquid form where it is formed, but further on, in very different quantities according to the surfaces it meets; hence the apparent contradictions between the results of gas-analyses and those of measuring the acid condensed on trays. The latter mode of observation is utterly worthless for deciding the question of the progress of the chemical reactions; this progress must undoubtedly be studied by gas-analyses. This last method presupposes that the gases in any special transverse section of the chamber are somewhat, although not absolutely, equally mixed; but that this is so, has been proved by the results of Lunge and Naef (see below) as well as by those of Mactear himself. The fact that nearly as much liquid acid is condensed on the trays near the top as upon those near the bottom of the chamber is easily explained by Abraham's theory of a spiral movement of the gases (see below), of which it is, indeed, a necessary consequence.

Hence we cannot accept Mactear's conclusion that the principal part of the acid is made in the upper portion of the chamber. In fact this does not agree with his own analyses of the chamber-gases, and even less with his further conclusion (p. 228 of his paper) that the principal condition is that of "having ample chamber-space, the form of the chamber not being so material." The argument that the sulphuric acid forming and falling rapidly towards the bottom of the chambers must displace the gases and force them to the upper portion is fallacious; for the volume of the acid forming is several hundred times less than that of the gases concerned in its formation, so that the above-mentioned action must be imperceptibly small.

Mactear's observations on the rate at which the acid is formed in different chambers of a set are very interesting. The following table shows the composition of the gases in the different parts of a set of chambers, connected with a Glover and Gay-Lussac tower, calculated from a long series of observations. In the original the figures are given to three decimals per cent., but we reduce them to one decimal, the estimations certainly not being accurate even to that place. The nitre in the original is all calculated as N_2O_4 , which is certainly wrong, and looking at the imperfection of former

analytical methods, we must accept the figures for nitre with all reserve.

	Gas entering the								Exit gas.
	Glover tower.	1st ch.	2nd ch.	3rd ch.	4th ch.	5th ch.	6th ch.	Gay-Lussac.	
SO ₂	6.3	6.3	4.5	2.6	1.4	0.7	0.3	0.03	0.03
O required to form SO ₃	3.2	3.2	2.2	1.3	0.7	0.35	0.11		
N equivalent to Fe ₂ O ₃ and SO ₃	45.6	45.2	46.6	48.0	48.9	49.4	49.7	49.9	50.0
O in excess air	9.4	9.4	9.7	10.0	10.2	10.3	10.3	10.4	10.4
N in excess air	35.5	35.8	36.9	38.0	38.7	39.1	39.4	39.5	39.6
N ₂ O ₁	0.12	0.12	0.13	0.13	0.13	0.13	0.13	0.01

The next table shows the comparative condensation of acid in the six consecutive chambers :—

No. of chamber.	Acid made.	H ₂ SO ₄ in acid made.	Excess water.	Percent. of H ₂ SO ₄ made in each chamber.
	Tons.	Tons.	Tons.	
1.	23.52	19.89	3.63	32.20
2.	22.59	18.68	3.91	30.26
3.	20.35	14.89	5.46	24.11
4.	10.23	4.35	5.88	7.04
5.	5.84	3.00	2.75	5.00
6.	2.19	0.86	1.33	1.39

The last table we take from Mactear shows the comparative condensation of the single chambers of various sets of sulphuric-acid chambers :—

Chamber 1.	31.50	32.20	32.5	38.4	34.1	33.8	52.4	63.9	38.7	78.6	53.9	81.8	26.1	32.1
" 2.	29.27	30.26	24.8	35.2	20.0	42.2	26.4	36.1	33.6	21.4	36.9	17.8	31.3	24.1
" 3.	18.71	24.11	19.3	15.6	19.7	22.6	16.5	...	12.9	...	9.2	...	20.4	17.1
" 4.	10.32	7.04	15.5	6.2	18.1	9.8	11.8	13.7
" 5.	6.45	5.00	5.8	3.2	7.3	3.4	7.0	5.4
" 6.	3.75	1.39	2.1	1.4	0.5	1.6	2.4	2.4
" 7.	0.3
Tunnels	1.4	4.7	0.4
	100.00	100.00	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.0	100.0

Probably the most extensive and complete investigation on the phenomena taking place in the vitriol-chambers has been made by myself in conjunction with Dr. Naef at the Uetikon Alkali-Works near Zurich, where a set of chambers was placed at our

disposal for this purpose during a space of several months. From our Report thereon (Chem. Ind. 1884, p. 5 *et seq.*) I have already quoted in several places, *e.g.* the methods employed for testing the gases (p. 333) and the observations of chamber-temperatures (p. 475). I here give a very short abstract of the important results obtained, which in all essential points have been entirely confirmed by a similarly extensive investigation made by Retter at a Hamburg works (Zeitschr. f. angew. Chem. 1891, p. 4 *et seq.*). The set of three chambers observed has been briefly described on p. 475. They were provided in twelve different places with complete sets of absorbing-tubes, large aspirators, and everything else required for making the most detailed and accurate analyses of the chamber-gases hitherto attained*.

The first six experiments proved decisively that in a *normally* working set of chambers, containing a plentiful supply, but no excess, of nitre, the last two chambers did not contain any nitrogen peroxide† whatever, but exclusively nitrogen trioxide (nitrous anhydride). It had been assumed by Berzelius, and later on by R. Weber and by Hasenclever that N_2O_3 is the real oxygen carrier, whilst most other chemists assumed this to be the part of nitrogen peroxide; but Berzelius altogether confused N_2O_3 and N_2O_4 , and Weber and Hasenclever, although they, of course, sharply distinguished between these two compounds, did not give

* It is true that even these analyses do not represent the absolute facts of the case. Some changes may, and even must, have taken place in the gases on their passage through the absorbing-apparatus; more especially the estimation of NO is not one of the most accurate operations. Nor can it be assumed that the samples of gas aspirated always represented the true average of that part of the chamber; and it was altogether impossible to be sure of following up one and the same batch of gas during its progress through the chambers. Our analyses cannot therefore pretend to be authoritative in all details, but they may certainly be taken as representing the general working of the process. Sorel's criticisms of our methods are not very well placed, as he does not suggest any better ones; his own plan of analyzing nothing but the drip-acids is altogether misleading, as it takes no notice whatever of the proportions of oxygen and nitric oxide in the surrounding gases; and as it seems, from his description of the process, that he measured the reducing power of the acid by running a solution of potassium permanganate into the vitriol, instead of *vice versa*, he must have found nitric acid even where none was present, as proved by me in 1877 (Ber. d. deutsch. chem. Ges. vol. x. p. 1074).

† To avoid repetitions, we do not distinguish between NO_2 and N_2O_4 , but call the mixture "nitrogen peroxide." "Hyponitric acid" is an antiquated expression.

any proof whatever of their assumption that the nitrous gas within the chambers is N_2O_3 , not N_2O_4 . The observations and analyses of Naef and myself for the first time gave a basis of fact to the statement that nitrous acid is the real oxygen carrier in the vitriol process. The assumption that the N_2O_3 , constantly found by us to be the only nitrogen oxide in the last two chambers, was really nothing but a fortuitous mixture of $2NO$ with $1N_2O_4$, is altogether excluded by the conditions prevailing; for in that case the oxygen present in great excess must have oxidized at least a great part of the NO into N_2O_4 during its passage through the chambers and testing-apparatus, and, what is even more important, it is practically impossible that the gases by mere *chance* should have always consisted of a mechanical mixture of precisely 2 vols. NO to 1 vol. N_2O_4 . These observations have therefore clearly established the fact that *in a normally working chamber no nitrogen peroxide is found*, and Retter's observations (comp. p. 487) have entirely confirmed this. It is true that it was impossible to distinguish entirely between the single nitrogen oxides in the *first* chamber, as unfortunately no analytical methods are known by which this could be done in the presence of the large quantity of SO_2 existing in that place; all that can be done is to *calculate* the nitrogen oxides either into NO and N_2O_3 , or NO and N_2O_4 . But that only the former, not the latter, is admissible, is proved by our further experiments, which showed that even when abnormally N_2O_4 was produced in the third chamber, yet the second chamber never contained any N_2O_4 . *A priori* it is also most unlikely that in the first chamber, where the reducing action of SO_2 is so much more potent than in the second and third chamber, the nitrogen should be in a higher state of oxidation than in the latter chambers. It is therefore to be considered a fact *that the nitrogen oxide present in the last chambers is essentially nitrogen trioxide, accompanied in the first chamber by nitric oxide, NO .*

Another set of five experiments was made in this manner, that the quantity of nitre was increased far beyond the normal measure, so that a large volume of yellow vapours escaped from the Gay-Lussac tower. Under these anomalous circumstances, nitrogen peroxide was found in the third, but never in the second chamber. *The chambers therefore contain nitrogen peroxide only when the supply of nitre is abnormally high.* The formation of N_2O_4 must be regarded as a secondary reaction, brought about in the following way. With an abnormally high supply of nitre the oxidation of

SO_2 into H_2SO_4 is almost entirely finished in the first chambers, as far as it can be driven (which is never up to the entire extinction of SO_2). There is hence very little sulphuric acid floating about as mist in the last chamber, and there is thus no impediment to the oxidation of NO going on to N_2O_4 , which, as we shall see in Chapter IX., does not take place in the presence of sulphuric acid. Moreover, the SO_2 still present in the cases here treated is of such minimal quantity (0.0004 to 0.002 per cent.), that its reducing action can scarcely be expected to be felt. The conclusion to be drawn from all this is that *nitrogen peroxide, being absent in normally working chambers, cannot take any essential part in the formation of sulphuric acid in the vitriol-chambers.*

When speaking throughout this work of "normally" and "abnormally" working chambers, I mean those terms as understood at all English and German works, with a chamber-space of at least 16 cubic feet per lb. of sulphur. In the "forced style" (*production intense*) practised at a few French works, where so much acid is produced in the chambers that only 12 cubic feet of chamber-space are allowed per lb. of sulphur, an excessively large supply of nitre must be given, which at all other works would be called "abnormally high," but certainly is not so under those exceptional circumstances. This leads to the regular appearance of nitrogen peroxide in the last chamber, and perhaps even of nitric acid in the nitrous vitriol of the Gay-Lussac tower. Sorel's statements in this respect are made uncertain by the fault in the analytical method employed by him (comp. above, p. 487, footnote), which would tend to make the proportion of nitric acid larger than it was in reality.

Special experiments made by Lunge and Naef proved the following important facts:—1. Even with an abnormally low percentage of oxygen in the exit-gases (4 per cent.) the formation of N_2O_4 takes place when an excess of nitre is sent into the chambers. 2. Even with an abnormally high percentage of oxygen in the exit gas (8.18 to 9.19 per cent.) no N_2O_4 is formed when the supply of nitre has been a normal one. This shows that *the quantity of air sent into the chambers has no influence whatever upon the formation of nitrogen peroxide*, which, on the contrary, is *exclusively* caused by an excess of nitre.

In Lunge and Naef's paper there follow experiments on the losses of nitrogen compounds, which will be mentioned later on, and then experiments on the *distribution of the gases and the*

progress of the process in the chambers. For this purpose there were eight sets of absorbing-tubes fixed in various parts of the chambers, three of which were always worked simultaneously; in each place at least 20 litres of gases were aspirated for every test, the whole being finished within 5 or 6 hours. Five different complete sets of such observations were made, comprising both normal working and shortness of nitre in the chamber.

It would be too lengthy to give all the details of the analyses; they prove the following facts. When the chambers are working in a *normal* way, the percentage of SO_2 in the gases decreases very quickly, and in the middle of the first chamber has already fallen from 7 to 1.7–1.9 per cent., so that about 70 per cent. of SO_2 must have been converted into sulphuric acid. From here to the end of the first chamber there is very little action, and only 4 per cent. of the original SO_2 is here absorbed. When entering into the second chamber the reaction is suddenly revived, and in its middle the gases contain only 0.2 to 0.4 per cent. of SO_2 , 20 per cent. of the initial SO_2 being absorbed here.

From this point to the end of the set the oxidation proceeds very slowly, and never to the point of absolutely extinguishing the SO_2 . The diagrams, figs. 183, 184, show this both for the normal working order (in the thick line) and for working short of nitre (the thin line)—the horizontal lines corresponding to the length of the chambers, the perpendiculars to the percent. oxidation of SO_2 into H_2SO_4 . There is also a dotted curve added,

Fig. 183.

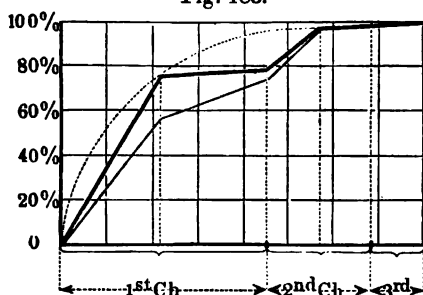
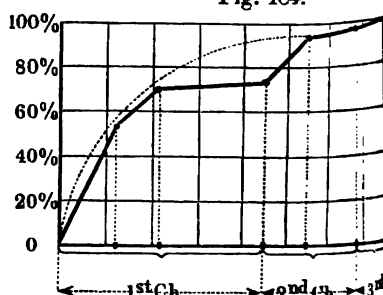


Fig. 184.



representing the progress of the process according to Hurter's theory (Chapter IX.), which is seen to agree much better with the normal than the anomalous style of working. This agreement comes out still better in fig. 184, representing the results obtained with another, intermediate, testing-place.

These experiments for the first time established a fact, subsequently confirmed by all similar observations, the whole importance of which will appear only in Chap. IX., viz., that the *conversion of SO_2 into H_2SO_4 takes place very quickly as far as the middle of the first chamber, then slackens very much, but is suddenly revived when the gases pass from this into the next chamber.* This fact was at the time explained merely by a better mixture of the gases, but we shall see that this explanation should be supplemented by other, and perhaps even more important considerations.

The observation made by Lunge and Naef at the Uetikon works, that the reactions after slackening in the last part of the first chamber experience a sudden revival when the gases pass into the next chamber, has been confirmed by later observations of Naef's at the British Alkali Works at Widnes (Chem. Ind. 1885, p. 285), by Schertel at the Freiberg Works (*ibid.* 1889, p. 80, und Sächs. Jahrb. f. Berg- und Hüttenwesen, 1890, p. 138), by Sorel (Zeitschr. f. angew. Ch. 1889, p. 270), and Retter (Zeitsch. f. angew. Ch. 1891, p. 4), and this must be looked upon as an established fact, the consequences of which for the theory of the nitriol-chamber process will be drawn in Chap. IX.

	1.			2.		
	a.	b.	c.	a.	b.	c.
O	9.63	10.37	8.45	5.15	5.62	5.18
N	89.90	88.80	90.64	92.05	92.26	92.47
SO_2	0.47	0.73	0.91	2.28	1.99	2.18
NO	0.05	0.06	0.06
N_2O_3	0.10	0.09	0.11

	3.			4.			5.		
	a.	b.	c.	a.	b.	c.	a.	b.	c.
O	6.68	6.07	6.04	5.98	—	5.42	6.37	6.27	6.27
N	91.28	91.84	91.90	92.64	—	93.17	91.77	91.70	91.76
SO_2	1.86	1.94	1.88	1.20	—	1.20	1.86	2.03	1.97
NO	0.07	0.06	0.06	0.06	—	0.06	—	—	—
N_2O_3	0.12	0.09	0.12	0.12	—	0.14	—	—	—

Another set of experiments referred to the question *how far the gases get mixed up in this progress through the chamber.* For this purpose the gas was aspirated and tested simultaneously from three places, lying in the same vertical line in the side of the first

chamber, with the results given in the table on the preceding page (a =top; b =middle; c =bottom).

The differences in composition found between a , b , and c here are certainly but slight.

For the following experiments three lead tubes were passed through the chamber-top in the centre line, on the same cross section as the place on the sides on which the points a , b , c , were situated, the three inner tubes reaching down to the same vertical height as the points a , b , c . Gas tests were taken at all six points at the same time, with the following results:—

	<i>a.</i> Top.		<i>b.</i> Middle.		<i>c.</i> Bottom.	
	Inside.	Outside.	Inside.	Outside.	Inside.	Outside.
Exp. A.—O	7.34	7.12	7.76	7.36	6.93	7.39
N	90.43	91.07	89.98	90.78	90.71	90.85
SO ₂	2.03	1.66	2.06	1.67	2.18	1.58
NO	0.08	0.08	0.08	0.10	0.10	0.10
N ₂ O ₃	0.12	0.08	0.11	0.09	0.07	0.08
Exp. B.—SO ₂	2.20	1.46	2.03	1.82	2.04	1.95

The differences in the composition of the gases here also is much slighter than was formerly assumed. More especially it was found that, contrary to former theories, the SO₂ is almost uniformly distributed at top, middle, and bottom. But it must be noticed that there was, without any exception, considerably less SO₂ found at the outside places, near the chamber-walls, than in the centre of the chamber. This was noticed by Lunge and Naef at the time (*l.c.* p. 17); they distinctly state that it proves that the reaction between SO₂ and O is rather stronger near the walls than in the centre of the chamber. A full explanation of this fact was only given several years later by Sorel's theory (Chap. IX.).

A last set of tests, in three places one above another in the first quarter of the first chamber, showed:—

	Exp. A.			Exp. B.		
	Top.	Middle.	Bottom.	Top.	Middle.	Bottom.
O	6.50	6.26	6.79	5.89	6.07	5.81
N	90.34	90.13	90.14	90.70	90.31	90.86
SO ₂	3.07	3.61	3.07	3.71	3.62	3.33

The entering gases had contained 6.6 per cent. SO_2 , so that at this place already about 50 per cent. of the SO_2 has vanished only 30 feet from the front end of the chamber.

All these experiments (with which the observations of temperatures, p. 475 et seq., agree) prove that the gases within the chamber are very quickly mixed up, whatever may be the cause of this, but that the mixture is not an absolutely equal one; there is always more SO_2 in the central part of the chamber than on the outside, or at top and bottom. Retter (comp. p. 487) confirms this.

It must be especially insisted on that the differences between the analyses of various samples of gases are far greater than can be accounted for by analytical errors or by the inaccuracy of the methods; it was distinctly proved that in some parts of the same transverse section there is more SO_2 , in some more O, in some more nitre, and it must be inferred without a shadow of doubt that there is in some places more moisture than in other parts of that section. Anybody who has experienced the difficulty of completely mixing two currents of gases even when experimenting on a very small scale will consider this as a matter of course. Those, therefore, who contend that Lunge and Naef's analyses prove an absolutely uniform composition of the gases in the same section of the chamber, and who from this infer the uselessness of a more intimate mixture, are altogether wrong, the above contention being erroneous; Schertel himself (Sächs. Jahrb. 1890, p. 144), who had formerly adhered to the just-mentioned opinion, afterwards found that the mixture of the gases is not at all absolutely perfect.

Thus Lunge and Naef's observations have refuted all the various theories according to which the sulphuric-acid making process is either taking place principally close to the bottom-acid (H. A. Smith) or immediately below the top of the chamber (Mactear). They are, however, altogether compatible with Sorel's theory (Chapt. IX.), which demands a stronger formation of acid near the chamber-walls, and with the theory of Abraham (Dingl. Journ. 1882, vol. 245, p. 416), concerning *the path on which the gases travel within the chambers.*

After refuting the opinion pronounced by Schwarzenberg, according to which the burner-gases at once rise to the top of the chamber, and then gradually sink down in nearly horizontal layers, Abraham states his own views as follows:—The burner-gas, on

entering the first chamber, meets a gaseous mixture whose temperature and composition differs but little from its own; it therefore spreads all over the front part of the chamber from top to bottom, and is slowly propelled by the draught along the chamber all over its transverse section. The formation of sulphuric acid also takes place regularly and equally at all points of each transverse section, taken at right angles to the length of the chamber, first rapidly, then more slowly. (This cannot be right if Sorel's theory be accepted.) The heat produced by the reaction raises the temperature of the interior, whilst at the side walls and the tops this heat is carried off by radiation outside. Thus is produced a difference in the temperature and the density of the gases which must lead to their rising in the centre of the longitudinal section, and to their descending along the sides of the chamber. Since the cause of this difference of temperature is a constantly acting one, the just described movement goes on through the length of the chamber, and is modified only at the ends, both through their own cooling action, and through the contraction of the current produced by the connecting-pipes. Thus *the gases travel in vertical layers at right angles to the length of the chamber, from the front to the back end, but each single gaseous molecule describes a spiral line, whose axis is parallel to the length of the chamber.*

This is of course only a general expression of the path of the gases within the chambers, to be modified locally by special circumstances; but it accounts for the approximate equality of the composition of the gases and temperatures observed in Lunge and Naef's and even in Mactear's experiments; Abraham's conception may therefore be accepted as an approximation to the truth.

It is generally assumed by practical men that *carbonic acid* exercises a very injurious action in the lead chambers, and it is principally on this account that "coal-brasses" are rejected as raw-material for the production of sulphuric acid (p. 34). If this is really the case, it is all the easier to understand why the proposals for filling the lead chambers with coke have been unsuccessful (p. 376). The reason why it should be so is not yet clear. Some practitioners assume that the CO_2 forms distinct layers, preventing the intimate contact of the gases with each other and with the bottom-acid; but I am not aware of any direct observations on this point, except in one case where blende containing

very much carbonates was worked, when it was found by many gas-analyses that the carbonic acid accumulated in the corners and other "dead" places, whilst the main stream of the gases contained much less CO_2 . This subject ought to be further investigated, especially as I know of a Bohemian works where sulphuric acid is made from material containing 10 per cent. of bituminous substances, without any special trouble being experienced.

Testing the Chamber-exits.

Apart from the ultimate check on the process afforded by frequent estimations of the yield of acid and the consumption of nitre, of which we shall speak later on, it is very desirable, and is indeed now required by law, to control the quantity of acids escaping from the vitriol-chambers into the atmosphere. As far as "low-level escapes" are concerned, that is the gas blowing out of pyrites-kilns, potting-holes, accidental leaks in the chambers, and so forth, it is not possible to estimate them directly; but it is just these kinds of escapes that are most readily perceived, and although they may be very troublesome to those residing in the immediate neighbourhood, they hardly ever amount to any considerable percentage of the sulphur burned.

It is very different with the gases escaping from the end of the whole system into the atmosphere, whether it be through a simple pipe or a Gay-Lussac tower, or the chimney. These "high-level escapes" may cause a serious manufacturing loss, and they may also amount to a real nuisance for a somewhat wide circle round the works, although generally only temporarily, especially in unfavourable weather. Before the introduction of nitre-recovery apparatus these losses, both of the acids of sulphur and those of nitrogen, must have been far more considerable than now, as the whole style of working inevitably tended to this (comp. p. 463); but nothing certain can be stated with regard to this, as no observations on the acidity of chamber-exits were formerly made, and at present all well-arranged works do recover their nitre. In this case the losses will not be quite so serious, but they do exist all the same, and that to a greater extent than was formerly supposed.

Among the first who drew attention to the necessity of regularly testing the chamber-exits for their acidity were Mactear (Chem. News, v. 36, p. 49) and G. E. Davis (*ibid.* v. 41, p. 188).

Control of the acids escaping from the chambers into the atmosphere has been made compulsory in England, since, in 1881, it was enacted by law that the total quantity of sulphur acids escaping from an alkali-works should not exceed four grains per cubic foot, expressed in terms of sulphuric anhydride, SO_3 , (Sec. 8 of the Act). About nitrogen acids or nitric oxide nothing is enacted, probably because the quantity escaping from alkali-works is never so great as to cause a nuisance, but it is all the more important for the manufacturer himself to know how much nitre he is losing in this shape; moreover, in testing the chamber-exits it is but little additional trouble to include the nitrogen acids.

The Government Inspector's Reports show that the real escape of acid gases from the exits of sulphuric-acid works is far below the maximum prescribed by the act. The acids escaping, calculated in grains of SO_3 per cubic foot, were in 1887, 1.500; in 1888, 1.490; in 1889, 1.370.

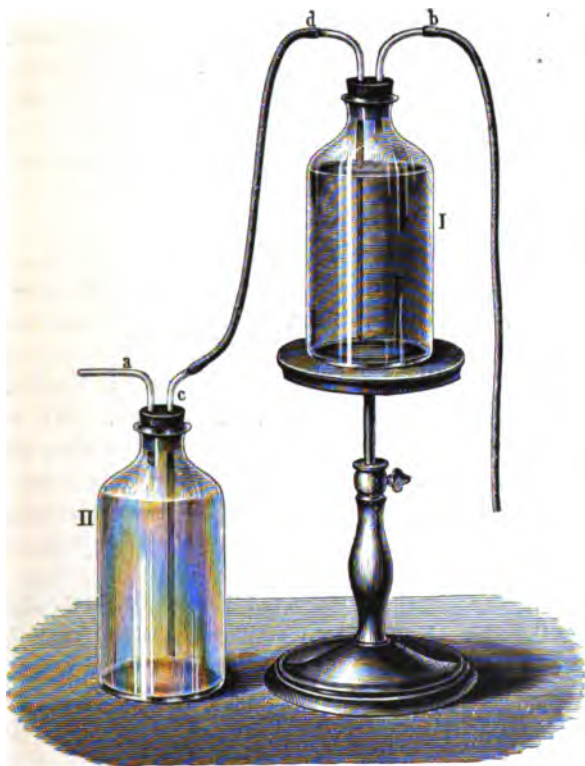
Two systems may be employed for controlling the acid escape, that of taking several separate tests through the day, and that of continuously aspirating some of the gas through a set of absorbing-apparatus, and measuring the quantity of gas passed through them.

The unreliability of the first system is too patent to be enlarged upon; it is hardly applicable at all to night-work, to begin with. Hence the continuous-testing system has been generally adopted, and this at many works in the very complete shape given to it by Mr. Mactear (*loc. cit.*). His apparatus consists of a water-jet pump (of the system invented by Dr. Sprengel, but commonly called "Bunsen pump") for aspirating the gases, a set of absorbing-tubes, and a gas-meter to measure the volume of the residual gases after absorption. The whole, including the cocks and connections, is enclosed in a locked closet to prevent their being tampered with. The meter is fixed with an index so arranged that by observing the reading for one minute the rate of passage per hour is given by direct indication, so that the rate of aspiration is easily arranged. Mactear at that time proposed caustic soda and ammonia as absorbents, to be titrated for SO_3 with permanganate; but this would yield quite wrong results, far below the truth, as sodium sulphite is rapidly oxidized by the oxygen passing through the solution.

Mactear's apparatus is very efficient, but it is very costly, and any such delicate apparatus as a gas-meter is very liable to get out

of order in such proximity to acid vapours. Hence at most places cheaper and simpler forms of aspirators have been adopted. One of the simplest is represented in fig. 185. It consists of two glass bottles, I. and II., each provided with a twice-perforated india-rubber cork, through which passes one elbow-tube (*a*, *b*) ending just below it, and another (*c*, *d*) reaching down to its

Fig. 185.



bottom. The tubes *c* and *d* are connected with an elastic tube; another such tube connects either *a* or *b* with the absorbing-apparatus. One of the bottles, say I., is placed so that its bottom is raised above the top of II. If now *b* is connected with the absorbing-apparatus, and the air is sucked from *a* for a moment, the siphon formed by *c*, *d* and the elastic tube begins to run, gas

being aspirated from *b*. When the contents of I. are run out, the elastic tube is detached from *b*, the position of the bottles is reversed so that II. now stands higher, and the elastic tube is put upon *a*; the connection between *c* and *d* is not touched. Usually the siphon begins to act again of its own accord; otherwise it is started by sucking for a moment at *a*. The quantity of water running out of the bottles at each turn is determined once for all.

The plan just described has the drawback of requiring an attendant to change the position of the bottles, and is hence hardly convenient enough for continuous testing. For this purpose, if a meter is to be dispensed with, a vessel of large capacity, say several cubic feet, should be provided, sufficient to serve for 24 hours without special attendance. Such a vessel can be made of glass, stoneware, or wood lined with lead; it should be cylindrical and provided with a gauge for measuring the height of the water within; in order to act quite equally it should be on the principle of a Mariotte's bottle, as described on p. 405. The form adopted by Younger (*J. Soc. Chem. Ind.* 1887, p. 347) has no special advantages.

An excellent apparatus has been described by W. G. Strype (*Trans. Newc. Chem. Soc.* 1880, vol. iv. p. 357). We will here give a description of it, abridged from the inventor's own words, with two drawings, figs. 186 and 187, showing it in two different conditions; but it is unnecessary to say that some details, such as the absorbing-apparatus, may be varied without any detriment to the principle.

Fig. 186 shows it in the process of being charged with water and having the old solution removed; and in fig. 187 it is shown as in ordinary work. The measuring-vessel E is of some 5 cubic feet capacity. The supply of water to charge this vessel is through the cock A, communicating with the vessel by means of the large pipe B, C, which is carried up to the open end at D, and to such a height as to ensure that too much pressure is not thrown on the apparatus when it is being charged; if too much, of course the water will overflow at the open end D. The air or residual gas remaining in the measuring-vessel after each period of absorption escapes, when it is being refilled, through the tube *a a' a''* into the lower vessel F, under the pressure of a small head of water of about one foot, and as the escaping air communicates by means of

Fig. 186.

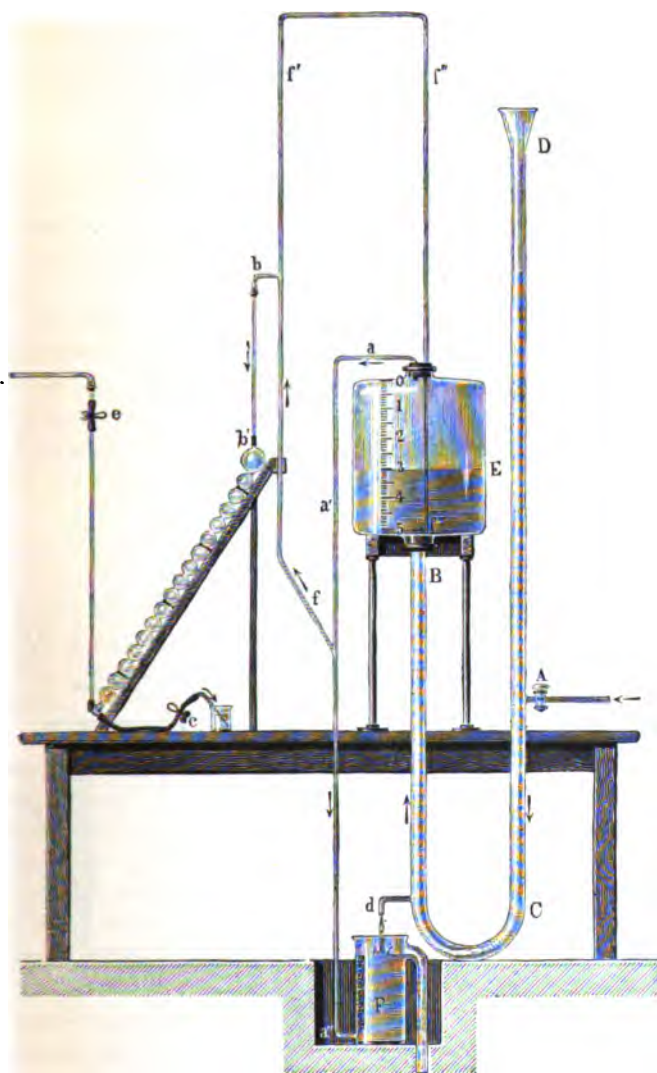
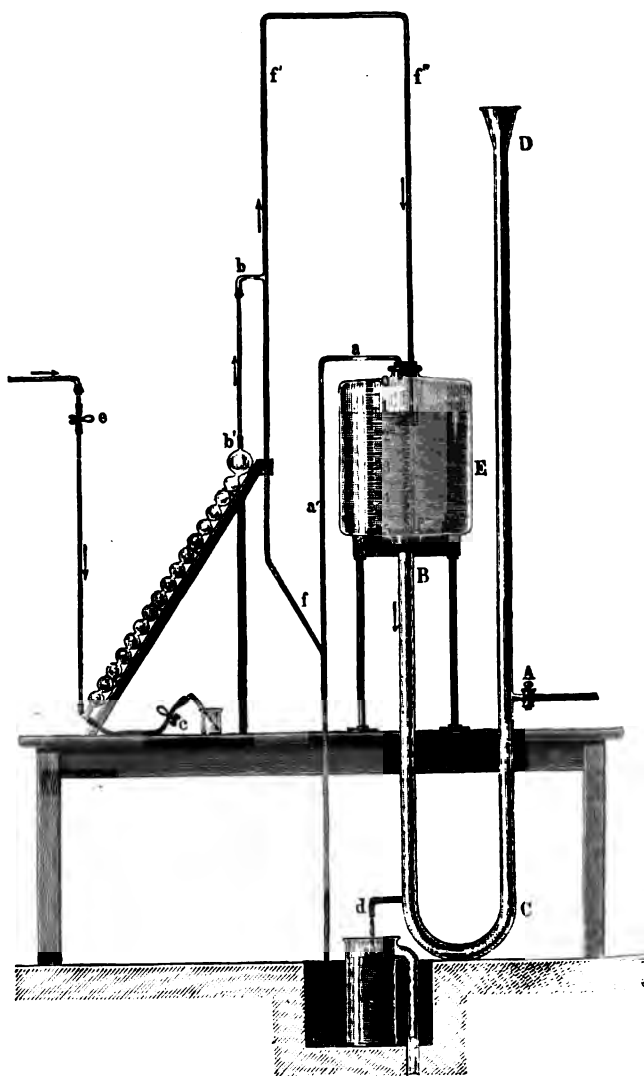


Fig. 187.



the tube *fb b'* with the test-bulbs, the pinch-cock at *c* being opened, the small pressure thus expels the old absorbing-solution as shown in fig. 186. When the vessel *E* is full, the old absorbing-solution being driven out of the bulbs, the cock *A* is shut, and the excessive water drains away from the small drip-pipe *d*, thus emptying all the connections to the condition shown in fig. 187; and the pinch-cock at *c*, and also the regulating pinch-cock on the pipe at *e*, which communicates with the chamber-exit, being closed, the flow ceases, and equilibrium is established by the apparatus being under the small vacuum due to the head of water in the vessel *E* over the open drip-pipe *d*. The pinch-cock *c* is now opened, and the india-rubber tube hanging from it is dipped into a beaker containing the test solution, which is now drawn up into the bulbs by the vacuum. When the charge is complete the pinch-cock at *c* is closed, and the regulating pinch-cock *e* opened to the required extent so as to admit the escaping gases from the chamber-exit to enter the apparatus; and absorption of the acids follows, together with accurate measurement of the volume dealt with; the residual gas passes into the measuring-vessel through the tubes *b' b*, *f' f'' f'''*. The latter tube is carried down at *f'''* close to the bottom of the vessel *E*, in order to secure a uniform flow of gas with the varying head due to the gradually diminishing level of water in the vessel, in the manner too well known to need further reference, and it is to secure this point that a difficulty arises in arranging such an apparatus. The tube *a a' a''* must be sealed off when the apparatus is at work if the flow of escape through the absorbing solution is to be at a uniform rate, and this is accomplished by a very simple plan. Upon turning on the water at *A* to charge the apparatus, the water runs down *a a'*, and when as low as the inclined pipe at *f*, air glides upwards, and the small quantity of water in the inclined pipe *f* also drains away; without this contrivance there would be a small quantity of water driven over into the test-bulbs each time the apparatus was charged, but the tube being placed in a diagonal direction entirely prevents this.

The proportions and relative positions of the various parts are accurately shown to scale on the drawing, and it is important this should be carefully attended to in constructing the apparatus.

The arrangement to contain the absorbing-solution consists of a series of 30 bulbs, each about $1\frac{1}{8}$ inch diameter, with small and short necks between them (the bulbs are made in sets of 10 each,

and three sets are coupled together with small pieces of india-rubber tubing, and the charge of 300 c.c. occupies about 22 of them, leaving a little free space in the upper part of each. A large bulb of some 4 inches diameter is placed, as shown, at the head of the bulbs, to catch any of the absorbing-solution in case it should be drawn up through all the smaller bulbs by accidentally turning on the flow of gas with too much violence in starting the apparatus. The solution used in this way contains 100 c.c. normal caustic soda, diluted to 300 c.c., coloured with litmus*. The drain-pipe *d* is always open and is of small aperture, but sufficient to more than carry away the water as it drains from the measuring-vessel in ordinary working, and thus a constant vacuum is maintained.

The apparatus is preferably constructed of glass, with india-rubber junctions; but of course it can just as well be made with an iron or lead measuring-vessel and lead pipes, a water-gauge being employed to observe the level of the water in E.

The staunchness of all the parts is ascertained, when the apparatus has just been charged, by shutting off the pinch-cocks *c* and *e*, and seeing that no water drains from the open pipe *d*. In charging, the water freely flows from *d*, but the aperture being small this does not appreciably interfere with the filling of the vessel E.

Whatever be the system of aspirating the gases, they must be passed through certain *solutions to absorb the acids* contained therein as completely as possible. The different acid compounds of sulphur are estimated together, as well as those of nitrogen, whatever degree of oxidation they may possess. The following *prescriptions* agree in the main with those published by the *British Alkali Makers' Association* in 1878; they are recorded in Lunge and Hurter's 'Alkali Makers' Pocket Book,' 1st edition, pp. 86, 87. A continuous test over 24 hours is taken of the gases escaping from the exit-pipes of the Gay-Lussac towers, aspirating at least one cubic foot per hour by means of any aspirator acting at a constant rate, and recording the volume of gas ($=V$) by means of gauging the aspirator or by a gas-meter. The volume *V* is reduced to

* Methyl-orange should *not* be used in this case, as it is destroyed by the nitrous acid present.

0° C. and 760 mm. pressure (= 32° F. and 29.92 inches) by the tables contained in the 'Pocket-book,' pp. 28 *et seq.* *, and is now called V'. In order to allow comparisons, the number of cubic feet of chamber-space per pound of sulphur burnt and passing into the chambers is recorded, excluding towers, but including tunnels, the amount of sulphur being taken by the weekly average, stating the distance of the testing-hole from the point at which the gases leave the Gay-Lussac towers. The absorption-apparatus consists of four bottles or tubes, containing each not less than 100 cc. of absorbing-liquid, with a depth of at least 3 in. in each bottle, the aperture of inlet-tubes not to exceed $\frac{1}{30}$ inch in diameter and to be measured by a standard wire. The first three bottles contain each 100 c.c. of normal caustic-soda solution (31 grammes per litre), the fourth 100 cc. distilled water. The caustic soda must be free from nitrogen acids. The gases are tested (1) for total acidity, stated in grains of SO_3 per cubic foot of gas, or else in grammes per cubic metre; (2) sulphur acids; (3) nitrogen acids—both stated in grains of S and N per cubic foot (or grammes per cubic metre). The analysis is carried out as follows:—The contents of the four bottles are united, taking care not to unnecessarily augment the bulk of the liquids, and are divided into three equal parts, one of which is reserved for accidents &c. The first part is titrated with normal sulphuric acid (49 grammes H_2SO_4 per litre) to ascertain total acidity. The number of c.c. of acid necessary for neutralization is called x . The second part of the liquid is gradually poured into a warm solution of potassium permanganate, strongly acidified with pure sulphuric acid. A small excess of permanganate must be present, and must be afterwards reduced by the addition of a few drops of sulphurous-acid solution, until only a faint red tint is visible. Now all nitrogen acids are present as HNO_3 , but no excess of SO_2 . The HNO_3 is estimated by its action on FeSO_4 . 25 c.c. of a solution, containing per litre 100 grms. of crystallized ferrous sulphate and 100 grms. pure sulphuric acid, are put into a flask, 20 to 25 c.c. pure concentrated sulphuric acid is added, the mixture is allowed to cool, and the other mixture, treated with permanganate &c.,

* The law prescribes the cubic foot to be measured at 60° F. and 30 inches, which necessitates the use of other tables or factors than those mentioned in the text, but the difference is hardly perceptible, and is within the limits of experimental error.

is added. The flask is closed by a cork with glass tubes. A current of CO_2 passes through and issues beneath the surface of some water, to prevent entrance of air. First, all the air is expelled in this way by an apparatus evolving CO_2 by constant action; then the solutions are introduced, and the contents of the flask are heated to boiling, till the dark colour produced by the formation of NO has changed to a clear light yellow. This lasts a quarter of an hour to one hour, according to the quantity of HNO_3 present and that of the sulphuric acid added. The unoxidized ferrous sulphate is titrated by a semi-normal permanganate solution (yielding 0.004 grm. oxygen per c.c.); the c.c. used = y . Since the titre of the iron solution changes pretty quickly, it should be tested daily by taking out 25 c.c. with the same pipette as serves for the above-described operation, and ascertaining the amount of permanganate required for oxidizing it, = x c.c. The magnitudes sought are found by the following equations:—

1. *Total Acidity* in grammes per cubic metre:

$$\text{SO}_3 = \frac{0.120(100-x)}{V'}.$$

2. *Sulphur* in grammes per cubic metre:

$$S = \frac{0.008(600-6x-z+y)}{V'}.$$

3. *Nitrogen* in grammes per cubic metre:

$$N = \frac{0.007(z-y)}{V'}.$$

1. *Total acidity* in grains per cubic foot:

$$\text{SO}_3 = \frac{1.852(100-x)}{V'}.$$

2. *Sulphur* in grains per cubic foot:

$$S = \frac{0.12346(600-6x-z+y)}{V'}.$$

3. *Nitrogen* in grains per cubic foot:

$$N = \frac{0.10803(z-y)}{V'}.$$

If the nitrogen acids are not to be separately estimated (and the Alkali Act does not require this to be done), the above prescriptions can be extremely simplified. It is only necessary to employ the apparatus shown on p. 330, fig. 100, and intended for testing the burner-gases for sulphur acids, or else one of the absorbing-apparatus to be mentioned below is employed. The apparatus is charged with 100 c.c. of normal caustic-soda solution, coloured with phenolphthalein, which acts equally upon SO_2 and H_2SO_4 , and this is re-titrated with standard acid. The caustic-soda solution should be as free as possible from carbonate,

as CO_2 acts upon phenolphthalein as well. The formula for calculation is then No. 1 divided by 3, that is :—

$$\begin{aligned}\text{SO}_2 &= \frac{0.040(100-x)}{\sqrt{V}} \text{ grms. per cubic metre,} \\ &= \frac{0.617(100-x)}{\sqrt{V}} \text{ grains per cubic foot.}\end{aligned}$$

The shape of the absorbing-vessels is not at all indifferent. When employing ordinary bottles with simple glass tubes dipping below the liquid, the absorption is often incomplete, even if several bottles are used in succession, which causes considerable pressure. The use of very narrow inlet-tubes, as prescribed in the 'Alkali Makers' Instructions' (p. 503), lessens, but does not entirely avoid, the evil of incomplete absorption. The potash-bulbs used in

Fig. 188.

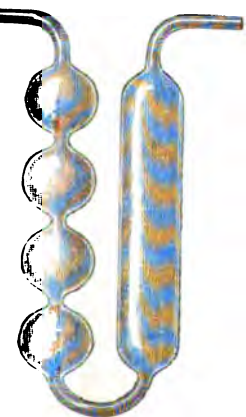


Fig. 189.

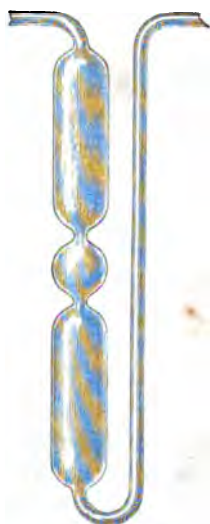


Fig. 190.



organic analysis cannot be employed, because it is too difficult to empty their contents without any loss.

The absorption is better when using Mitscherlich's tubes

(fig. 188), of which Todd's tubes (fig. 189) are but a slight modification. The shape of absorbing-bottle shown in fig. 190 serves also very well. Better than these is the Pettenkofer tube as modified by myself (fig. 191) and still better a 10- or 15-bulb-tube, as shown in fig. 192, one of which generally suffices for complete absorption.

Nitric oxide can be (and generally is) present in the gases after passing through the absorbing-bottles. It can be estimated in an absorbing-tube (fig. 191), or better in a bulb-tube (fig. 192),

Fig. 191.

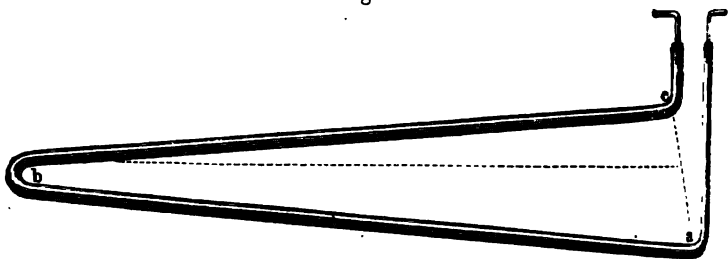
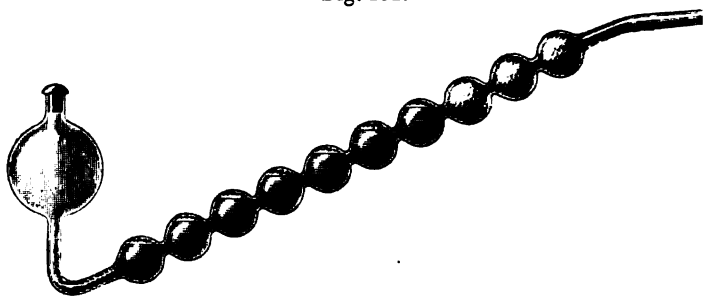


Fig. 192.



interposed between the tubes of the apparatus serving for estimating the acids and the aspirator. The bulb-tube is charged with 30 c.c. of seminormal permanganate solution and several c.c. of sulphuric acid. The gas is passed through for 24 hours, and the tube emptied and washed out. Now add 50 c.c. of ferrous-sulphate solution, corresponding to $2x$ permanganate (comp. p. 503), and re-titrate the decolorized liquid with permanganate. (If a precipitate of manganese peroxide has been

formed in the absorbing-tubes, rinse the tubes with some of the iron solution.) The quantity of the permanganate last used is called u . The NO has altogether consumed $(30 + u - 2z)$ c.c. of permanganate, giving:—

In grammes of nitrogen per cubic
metre of the volume V' .

$$N = \frac{0.007(30 + u - 2z)}{3V'}$$

In grains of nitrogen per
cubic foot.

$$N = \frac{0.10803(30 + u - 2z)}{3V'}$$

The quantity of nitric oxide present in chamber exit-gases may be at times rather considerable without attracting notice, as it oxidizes only very slowly when strongly diluted with inert gases. This makes some of the absorbents proposed, as hydrogen peroxide or a mixture of strong sulphuric with nitric acid, practically useless, as proved by myself by many laboratory experiments, in consequence of which the use of an acid solution of potassium permanganate and the apparatus described here were first proposed (in 1881). Even this process requires a very good absorbing-apparatus and a very slow stream in order to take all the NO out of the gases.

The apparatus and methods described by Lovett (J. Soc. Chem. Ind. 1882, p. 210) may be consulted by those specially interested in this subject, but call for no special remark here. This holds good also of the papers of G. E. Davis (Chem. News, vol. 41, p. 188) and Pringle (J. Soc. Chem. Ind. 1883, p. 58).

The gas collecting in the aspirating-vessel of any of the above-described apparatus, being an average sample of the exit-gases free from acids, is very conveniently employed, in preference to samples taken at random over the day, for *estimating the oxygen* contained in the exit-air. This estimation has been previously described (p. 330), and we have here only to show how the estimation of oxygen in the exit-gas may be used for *finding out the quantity of sulphur burnt*, expressed in grams per litre of the exit-gas, so that the quantity of sulphur lost in that gas may be put in direct comparison with the total sulphur used. For this the following formula has been proposed by me in Dingler's Journal, vol. 226, p. 634:—

$$(20.95 - a) \times 0.009637 \times \frac{1}{1.00367} t \times \frac{h}{760} = x.$$

Here a denotes the percentage of oxygen in the exit-gas, t its temperature, h the barometrical pressure in millimetres, x the total quantity of the sulphur actually burnt, expressed in grams per litre of the exit-gas; with this the quantity actually found should be compared, in order to find the percentage of loss. It should not be overlooked that no account is here taken of the sulphur remaining in the cinders.

CHAPTER VIII.

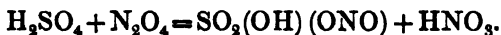
THE RECOVERY OF THE NITROGEN COMPOUNDS.

THE recovery of the nitrogen compounds which are still present in the gaseous mixture issuing from the last chamber has been previously mentioned as a process indispensable for the rational manufacture of sulphuric acid. It saves not merely at least two thirds of the nitre, but also a great deal (a quarter up to a third) of the chamber-space; it increases the yield of vitriol, and moreover prevents the escape of acid fumes into the atmosphere. Several processes may be employed for this object; but, with one exception, they only deserve a short mention. The only plan which has turned out successful in manufacturing practice, and which, certainly after a considerable length of time, has been introduced into all well-managed works, is that which was proposed by Gay-Lussac as early as 1827, viz. the *absorption of the nitrous fumes by strong sulphuric acid*. The chemical fact underlying this process, viz. the behaviour of the oxides and acids of sulphur and nitrogen towards one another, has been fully discussed in Chapter III. (p. 145 *et seq.*), to which we must refer. We shall here enter upon the technical means employed for realizing the possibility of recovering by far the greater part of the nitre contained in the exit-gases from the vitriol-chambers. We recall, therefore, only the following reactions.

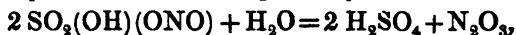
Moderately concentrated sulphuric acid absorbs from gaseous mixtures no *nitric oxide* except in the presence of oxygen, when of course higher nitrogen oxides are formed. *Nitrous acid* is absorbed with the formation of nitrososulphuric acid:



Nitrogen peroxide is absorbed with formation both of the just-named compound and of nitric acid:



Nitrososulphuric acid is *decomposed* by water alone :



or by water and SO_2 :



The most usual *apparatus for retaining the nitrous fumes* by means of strong sulphuric acid is the coke-tower, first employed in 1827 by Gay-Lussac, and justly designated everywhere by the name of its inventor. From the facility which this apparatus gives of retaining at least two thirds of all the nitre, and from the other important advantages realized by it (see p. 509), it might have been expected that it would have been generally introduced within a short period after its invention. But, most curiously, Gay-Lussac's invention was only carried out into practice for the first time in 1842, at Chauny; and forty years after its invention the majority of sulphuric-acid makers did not possess either Gay-Lussac's or any other apparatus for retaining the nitrous fumes; nay, even some of those who had adopted it in the first instance had abandoned it again.

The cause of this was that formerly the only plan of denitrating the nitrous vitriol obtained in the Gay-Lussac tower was by dilution, and that the expense of reconcentrating and of pumping the acid, &c. was thought to amount to nearly as much as the saving of nitre. Most manufacturers were not aware that the saving (which was mostly estimated too low, viz. equal to one half of the nitre) was not the only advantage of the absorbing-towers. But the great dearth of nitrate of soda which occurred about the years 1868-70 brought the matter vividly before them; at the same time on the Continent the composition of the chamber-gases, the chamber-space, &c. was studied more closely, and the advantage of an excess of nitrous gas in the chambers, which can only be secured by means of an absorbing-tower, became evident. These circumstances led to the re-erection of Gay-Lussac towers, and the more so as some few manufacturers had never given them up at all and had done very well with them.

In England, where the theoretical part of the subject has been much less attended to, another practical invention had in the meantime been made, which entirely removed the only essential drawback of the Gay-Lussac absorbing-tower, viz. the necessity of concentrating the acid; this was the *Glover tower*. Whilst little more than twenty years ago only a comparatively very small number of

English works absorbed their nitre-gas at all, since then all the larger and better works have introduced the Gay-Lussac absorbing-column, nearly always along with Glover's denitrating column. Probably some few exceptions may still survive; but we are here only speaking of works somewhat rationally managed. Even in 1873 very few English works' chemists were as depreciatory in their judgment, and at the same time as ignorant of the essence of Gay-Lussac's apparatus, as H. A. Smith showed himself to be in his pamphlet (Bode's translation, p. 82). His assertion that the Gay-Lussac tower was an outcome of negligence, since with greater care no loss of nitrogen compounds at all need be suffered, proves him ignorant of the reason why an excess of those compounds is purposely employed, which must afterwards be reabsorbed, viz. that the sulphurous acid may be fully oxidized. Directly after, he speculates in what way the sulphurous acid escaping "in the majority of works" may be utilized—a question which in working with the absorbing-tower does not exist, as such escapes are then too insignificant. The necessary answer to Smith's reasoning has been already given by his translator very thoroughly (*l. c.* p. 121, footnote).

Gay-Lussac's Absorbing-Tower for Nitrous Gas

consists of a chamber, placed at the end of the set of lead chambers, higher than wide (a "tower" or "column"), of which the walls are made of a material capable of resisting sulphuric acid, and the interior space is filled with a material presenting a large surface. By means of this "packing" a stream of sulphuric acid entering the column from above is divided into small drops; at the same time the current of gas rising up in the tower is divided into many small jets; and thus the contact between the gas and the acid, covering the surface of the packing, is multiplied. The principle applied here is exactly the same that had been employed for a long time in the "scrubbers" of gas-works, in order to deprive the gas of ammoniacal salts by washing it with water, and which is also applied to the condensation of muriatic acid in the decomposition of common salt (Book II.): it is always this, to produce a great many points of contact between the gas and the absorbing agent, and thereby to wash out the absorbable substance of the gas as much as possible; or the interior of the tower may be represented as a filter which allows only the inert gas to pass, but retains the gas acted upon by the absorbing agent.

The reason why such an apparatus is constructed in the shape of a tower or column (that is, why it is made much higher than wide) is this, that in the case of apparatus with a considerable horizontal section it is quite impossible to distribute a comparatively thin stream of the absorbing liquid equally over the whole section, and at the same time to force the gas to meet the liquid all over. Of course, the gas has always a tendency to rise where its way is not barred wholly or in part by a liquid; unless the columns are pretty narrow, it is not possible to prevent the liquid running down almost entirely in some places, the gas rising in others, so that but little of the two would come into contact, and the liquid would arrive at the bottom charged with very little absorbable matter, whilst the gas issuing at the top would still contain a good deal of it.

Hence follows this general principle:—An apparatus for the absorption of gas, such as are in question here, should be made no wider than is necessary in order that the draught may not be impeded by the packing; and the necessary cubical volume of the packing should be obtained by making the tower so much higher. Thereby another object is also attained—viz., the gas entering at the bottom of the tower, where it is richly charged with absorbable matter, meets a liquid containing already a good deal of the same, and therefore not capable of dissolving much more, unless an abundant supply is presented to it, which is just the case under these circumstances; on the other hand, the gas near the top of the tower, where it is almost entirely deprived of its absorbable parts, meets entirely fresh liquid, which is able to seize upon those parts even in a poor gas, whilst a partly saturated liquid would have no action upon such a gas. This is the theoretical explanation of the practical fact that a *saturated* absorbing liquid, along with *exhaustion* of the gas, can only be attained by building the towers very high.

A considerable vertical height of the absorbing medium can be also obtained by placing two towers alongside each other, and compelling the gas leaving the first tower at the top to pass downwards in order to rise again in the second tower. As a rule this arrangement is not to be recommended, for two reasons:—first, there is a loss of draught caused by compelling the gas to take the unnatural path downwards for a portion of its course, and the consequent great friction in the connecting-tube; secondly, in this way certainly the gas can be completely washed out, but

at the same time there does not result a saturated absorbing liquid, both of the towers having to be fed with liquid, which at the end only attains *half* the degree of saturation that would have been attained in *one* tower equal in height to both those employed and fed with a single jet. Only, where the strength of the absorbing liquid is of no consequence, it is often more convenient to employ two towers, one after the other, than one of double the height. With the large Gay-Lussac space recently employed by many works it is certainly found impossible to do with only one tower. In that case two towers are employed, the first being fed with the acid run down in the second after pumping it up again. An arrangement decidedly to be rejected is found in many books and in a few badly arranged works, where, from mistaken economy, the absorbing-tower is made of twice the usual horizontal section, and divided into two halves by a partition, in order to pass the gas up one half and down the other. The saving in cost as against two towers or a tower of double the height is not very considerable; on the other hand, that half of the tower in which the gas has to descend is almost entirely sacrificed, because here, where the gas and the liquid travel in the same direction, their mutual action, as experience shows, is very inconsiderable; both mostly travel downwards peacefully without interference and arrive at the bottom almost unchanged. The arrangement of a double tower is inadmissible unless the partition extends right through, and the gas issuing from the one division passes downwards by a special pipe, and is allowed to ascend again in the second division, and thus to *meet* the acid rain. This comes to the same thing as placing two towers alongside each other.

As far as the *width* of the absorbing column is concerned, it should be considerably wider than an empty tube of sufficient diameter for the current of gas, not merely because the packing of the tower occupies a large portion of its section and only leaves a small portion of it as clear space, but also because the packing must be purposely arranged so as to divide the current of gas into a great many separate jets, constantly changing their direction, and to expose them to the largest possible amount of *contact* with the surfaces of the packing wetted with the absorbing liquid. The tower must therefore be wide enough to take account of this purposely increased friction. Furthermore, it has to be considered that the *slower* the current of gas, the more time will

be afforded for the action of the absorbing liquid, and the more perfect the latter will be. This would lead to giving the tower as wide a section as possible, in order to slacken the speed of the gaseous current. As, for the reasons stated above, this plan cannot be carried out very far, the inference is that a certain middle path is to be taken: a tower should be made wide enough not to hinder the draught, and to leave sufficient time for the contact of the gas and the liquid, but not so wide that the liquid cannot be spread equally all over and that the gas can go past it. Evidently no exact calculations can be made as to the proper width; experience only can decide this point. Formerly it was assumed that ordinary coke-packed Gay-Lussac towers ought not to exceed 7 feet in width in order to secure a uniform distribution of the gas and the acids, but latterly towers up to 14 feet have been erected and no drawbacks are reported to have been caused by this extreme width.

The dimensions of the absorbing column necessarily correspond with those of the set of chambers it belongs to; its cubical contents should be *at least* 1 per cent. of the chamber-space. For sets of from 140,000 to 200,000 cubic feet the column might be 6 feet in width and 50 feet high; for a set of from 70,000 to 100,000 cubic feet a tower from 4 to 5 feet in width and 40 feet high is sufficient. In both cases it is best to give the tower an additional height of 10 feet; there will be all the more saving of absorbing acid the higher the tower and the longer the way for the acid. These statements refer to chambers working with pyrites; with brimstone the height of the tower need not exceed 26 feet.

Undoubtedly a larger absorbing-space, say 2 per cent. of the chamber-space, permits working with a larger economy of nitre than the above-stated sizes; in the case of large sets this space will mostly have to be divided into two towers. In fact, when the absorbing-space at the Jarrow chemical works was raised to 90 cubic feet per ton of pyrites per week, which amounts to about 2 per cent. of the chamber-space, the consumption of nitre was brought down from 1.45 to 1.05 part per 100 parts of pyrites. Similar results have been obtained elsewhere, for instance at Runcorn.

A table of the Gay-Lussac and Glover spaces in all Lancashire works is given on p. 373.

At Griesheim (Mon. Scient. 1889, p. 1235) the six ordinary Gay-Lussac towers, belonging to six sets of chambers, are supplemented by a large tower 30 feet wide, 10 feet long, and 30 feet

high, filled with coke. Acid of 142° Tw., comprising five-sixths of the daily produce, is employed for feeding this tower; it is divided by one large and six smaller distributors into 480 different jets. The weak nitrous vitriol produced in the large tower is employed for feeding the six ordinary Gay-Lussacs, and is generally brought up to a strength equivalent to 60 grams NaNO_3 per litre. In this way the waste of nitre has been reduced to 0.83 parts for 100 H_2SO_4 produced.

At the different works belonging to the Saint-Gobain Chemical Company (the largest in France) the real working-space (*i. e.* that occupied by the coke packing) of the Gay-Lussac towers formerly amounted to rather more than 5 cubic metres (say 180 cubic feet) per ton of pyrites burnt in 27 hours, or from 0.7 to 1 per cent. of the chamber-space. But recently this has been very much enlarged, and now amounts to 13 or 15 cubic metres (say 455 to 525 cubic feet) per ton of pyrites, or from 2 to 3 per cent. of the chamber-space, with a special view to "forced work" (p. 373). This does not comprise the space below the grates, that above the packing, and that occupied by the brick lining, whilst in most other statements the whole space within the leaden shell is counted.

The *foundations* of the tower must, of course, be very substantial, and, if possible, constructed in such a way that any acid running over will not damage them. It is preferred to make them high enough to avoid the gas from the last chamber having to descend towards the tower; if, however, the chambers are very high above the ground, this would involve considerable difficulty and expense, and the tower is then raised only high enough above the ground to leave a natural fall from its bottom to an acid-tank, and from this to the pumping-apparatus for the nitrous vitriol.

The foundations usually consist of a solid block of brickwork or stones, or else of two strong pillars surmounted by an 18-inch arch. Sometimes cast-iron columns are employed, on which are placed iron girders, and crossways on these iron T-shaped bearers (usually railway-rails), close together so as to form a continuous platform. These (as well as any brick- or stone-work) must be well painted with (frequently renewed) tar-paint, and must be covered at the top by a leaden apron which directs all the drips past the pillars into a safe place, where the foundations or pillars

cannot be touched by it. (The same plan should be followed with the foundations of Glover towers.)

The *framework* of Gay-Lussac towers is sometimes made of angle-iron, but much more usually of timber. In the case of towers of an angular section such frames are constructed in the usual way, as is seen in our diagrams of Gay-Lussac towers. Circular towers of moderate section are best made with a frame of four uprights, placed in the corners of a square; to these, at every 6 feet of height, metal brackets are fixed; from these are suspended, by means of hooks, broad iron hoops (say 3 inches wide, which closely gird the tower and support its lead shell. Wide towers are built like circular Glover towers (see below).

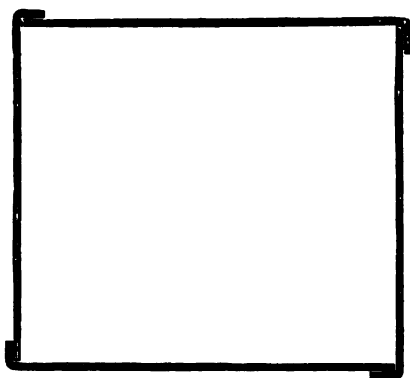
The timber frame must be kept clear of the lead, just as in the case of the vitriol-chambers (p. 342); this, of course, is even more necessary in case of the Glover tower (see below).

In most cases the absorbing-tower is made of lead and packed with coke. The lead in continental works is often made unnecessarily thick, from 14 to 28 lb. to the square foot; in British works it is often no more than 7 lb. or even 6 lb. to the square foot like the chamber-lead. It is, however, better to make it of 8-lb. lead, the bottom being a pound or two stronger. There is no reason why the lead should be stronger than this: the gas, as well as the acid, in this apparatus are only moderately warm, and, indeed, ought to be as cool as possible; nor is the lateral pressure of the coke, if properly packed, so great that it need cause any fear. At any rate the lead sides are necessarily supported by a frame. Both circular and square towers are found; the former take less lead for the same area. They are frequently lined inside with bricks, which are put in dry along with the packing; "split bricks" of 1 inch thickness are often employed for this purpose, lest too much space should be lost. The object of this lining is to prevent the coke from cutting the lead in settling down. It seems hardly worth while to go to the expense of the lining, and at the same time to lessen the area of the tower, for such a small matter, which can be easily remedied by putting on a patch of lead; the lateral pressure of the coke would only be avoided by making the lining 9 inches thick, which is rarely done, as it wastes too much space.

In the case of square towers, the sheets forming the sides should be in one piece from top to bottom, and should be turned over at

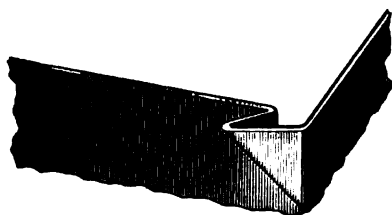
the corners in order to make a joint with the next sheet (fig. 193). The overlaps of the seams must, in every case, be placed outside

Fig. 193.



(also in the case of the Glover tower); otherwise they would be quickly destroyed. The bottom is made of a single sheet, the four edges being turned up to form the upstand. The corners are not cut out and burnt, but they are simply folded up as shown in fig. 194.

Fig. 194.



Circular towers are built up of annular drums, one above the other, each being supported by straps nailed to the upright posts, or, preferably, fixed in such a way that the overlap of the seam is turned over three-inch iron hoops suspended from the uprights (p. 516). This plan at the same time protects the hoops and gives an excellent stay to the tower. If there are more than four upright posts, one, or more, of them must be left out during the building of the tower, to get the leaden drains in.

In the south of France octagonal Gay-Lussac towers are in use, built of Volvic lava, like a hydrochloric-acid condenser, without any lead shell.

All Gay-Lussac towers have an *internal filling* ("*packing*"), mostly consisting of *coke*. This material is generally (and was formerly universally) regarded as the best for this purpose, because its irregular shape and rough surfaces offer to the gas a very large area of contact with the liquid. An advantage of coke against other materials, as pieces of glass, earthenware, flints, &c., is also its comparatively light weight. But two advantages sometimes claimed for it are non-existent. One of these is, that coke, owing to its porosity, offers a great many internal surfaces for the contact between the gas and the liquid; but this is erroneous. In the first place, porous coke is worthless for a coke-tower, for which dense coke is indispensable; secondly, the pores would at once be filled with liquid, which thus would not come into contact with the gas passing outside. It is not owing to its porosity, but to its rougher, more irregular, and therefore much larger surface, that coke is preferable to broken glass or earthenware, &c.

It is necessary to be very careful in the selection of the coke. Gas-coke is of no use at all here, only the hardest-burnt oven-coke, giving a clear ring and as little porous as possible, of a silvery white, not of a dull black. It must be carefully packed and all dull black pieces rejected. First only the large pieces, a foot and upwards in length, are picked out; these are placed in horizontal layers directly over the grating of the tower, crossing each other if possible; each piece must be placed by hand, inconvenient as it is that the workman has to be lowered down from the top to the bottom of the tower, and must receive his material in the same manner. Thus the first third of the tower is packed; then come the pieces next in size; and for the last third the smaller lumps may be used, and may be simply emptied in out of baskets. Nothing, however, is allowed to go into the tower which has not been sifted on a riddle with three-inch holes. Unless a coke-tower is packed most carefully, either the draught through it will be impeded, or there will be too much way left for the gas, or, in the most frequent and worst case, the packing will be too loose in some places and too dense in others, and thus there will be bad absorption along with bad draught.

Soft porous coke has to be rejected for two reasons: first, it cannot support the pressure of the superjacent column without being crushed, thus stopping the draught; secondly, such soft coke

is soon acted upon by nitrous vitriol, and is ultimately converted into a thick paste; this is very bad for the draught, and may necessitate repacking the tower.

Another claim which has been made for coke must also be rejected as unfounded, viz., that it is not acted upon by the gases or liquids within the Gay-Lussac tower. On the contrary, I have shown (J. Soc. Chem. Ind. 1885, p. 31) that the reason why "nitrous vitriol" never, except under totally abnormal circumstances, contains any nitric acid, even when the gases entering into the tower had contained N_2O_4 , is this, that the coke reduces the nitric acid originally formed from the N_2O_4 to nitrososulphuric acid; this takes place slowly at ordinary temperatures, but very quickly and completely at slightly higher ones (30° to 40° C.).

In a subsequent investigation (Zeitschr. f. angew. Chem. 1890, p. 195) I have shown that the action goes further, and that nitrous acid is reduced by the action of coke to nitric oxide, with formation of carbon dioxide. It is true that at the ordinary, or at a slightly raised, temperature this action is but very slow; but even then it is quite perceptible, and at temperatures about 70° it becomes very strong (comp. Chap. III. p. 160). This no doubt accounts for some of the losses in the manufacture of sulphuric acid, and it would seem to speak in favour of employing a description of packing which is not acted upon by the nitre in any way. In fact, Mr. Benker has informed me that at some works the ordinary coke-towers must be repacked every year, and that in places where the coke-packing has been replaced by cylinders of hard stoneware, the nitrous vitriol is very much stronger than with coke-packing under similar circumstances.

Of course, dense coke is less acted upon than porous coke (as distinctly proved once more in my experiments); the latter does not even resist the action of pure concentrated sulphuric acid without disintegration. But in the end all coke is gradually wasted, and long before this is done to such an extent that the real loss of weight would make it necessary to replenish the tower, the mud formed by the disintegration of part of the coke stops up the draught to an intolerable extent. Flushing the tower with water is sometimes a remedy, but far from generally. With acid-proof packing such washing is more efficient, as with stoneware cylinders, and especially with "plate-columns" (see

below); the latter are also far more quickly repacked in case of need than coke-towers.

Sometimes, in the case of very tall towers, grates, made of iron rods cased in lead, have been interposed in two or three places, divided equally over the height of the tower, in order to carry the weight of the packing. But as the packing inevitably settles down, these grates are forced downwards and easily tear the sides of the tower. They are useless, and have gone out of fashion again.

The above general remarks must now be supplemented by the description of a few apparatus actually constructed. First, we shall give a description of the Freiberg coke-tower, from Schwarzenberg's 'Chemical Products,' pp. 384-390. Fig. 195 is a sectional elevation, fig. 196 a sectional plan of the apparatus used at Freiberg for the recovery of the nitrous compounds, on a scale of 1:100. Its principal portion is the lead tower K, 5 feet 7 inches wide and 26 feet 3 inches high, supported by a timber frame similar to that of a lead acid-chamber. The cover, however, is not burnt to the sides, but can be taken off. It consists of a wooden frame, lined inside with lead, with a flange standing up all round the edge; the latter, when the cover is put on, fits into a channel worked into the side sheets, which are turned horizontally over the crown-tree; by filling this channel with sand a tight lute is produced. On the bottom of the chamber a kind of grating is constructed of hard-burnt fire-bricks, consisting of parallel walls, forming channels of about 1 foot 8 inches in height. They are covered in such a way that between the covering-tiles empty spaces of about $2\frac{1}{2}$ inches remain, through which the gas can freely pass from below and the acid from above. On this grating the coke is packed, with which the tower is filled close up to the exit-tube N, the larger pieces at the bottom and gradually smaller ones towards the top. In order to put these pieces in more conveniently, three man-holes are made in the side, consisting of wooden frames lined with lead and made tight with putty at the joints. From the last lead chamber the gas arrives in the tower through the pipe J, passing on its way the valve-box L, which allows it to be taken away direct through the tube, without any interruption of work, in special cases—for instance, repairing or repacking the tower. For this object the valve *b* is opened and *c* is shut. If, on the other hand, the valve *b* is shut and *c* is open, the gas

first goes through the short pipe *d* into a small space projecting at the bottom of the tower along the whole of one of its sides; from this it divides itself among the channels below the grating, and then ascends through the coke; at the same time sulphuric acid of about 152° Tw. trickles down through the coke, absorbing the nitrous acid out of the gas, and carrying it down as a solution of "chamber-crystals" or "nitrous vitriol." The gas deprived of nitrous acid goes away through the pipes N and M, again passing a valve-box, O, which serves as a means for interrupting, by closing the valve *e*, the communication between the tower and the pipe M, if the gas is not to go through the tower, but direct into the pipe M.

The nitrous vitriol runs from the tower through a tube *f*, visible in the plan fig. 196, into a tank R, from which it goes into the denitrating apparatus.

For the observation of the colour of the gas before and after its passage through the tower, two glass panes are placed in each of the two valve-boxes L and O, opposite to each other; or a portion of each of the two tubes J and N may be made of glass. The gas ought to be of a ruddy colour before entering the tower, and perfectly colourless after leaving it. (It is a very good plan to make the "sight" in the shape of a narrow lead box, 6 or 7 feet long, with glass panes at the opposite small ends. In this case the colour is seen through a deep layer of gas, and any admixture of yellow vapours is much more easily discovered than with the ordinary small sights.)

Instead of the loose cover and fixed bottom of the Freiberg towers, most works prefer a fixed cover with a man-hole hydraulically luted and an independent bottom with upstanding sides, similar to a chamber-bottom. Instead of the grating made of fire-bricks, many works have a kind of dry arch (see below). In a few cases iron rods covered with lead are used; but these cannot be recommended, as the lead may be cut in some places and the iron would then be acted upon.

At the Freiberg works the Gay-Lussac towers are connected with a chimney. This is almost indispensable where the gases have to travel a long distance in a pipe from the last chamber, which, of course, impairs the draught, but is otherwise a very good plan for cooling and drying the gases. It is even more necessary where there are two Gay-Lussac towers combined. But we dis-

Fig. 195.

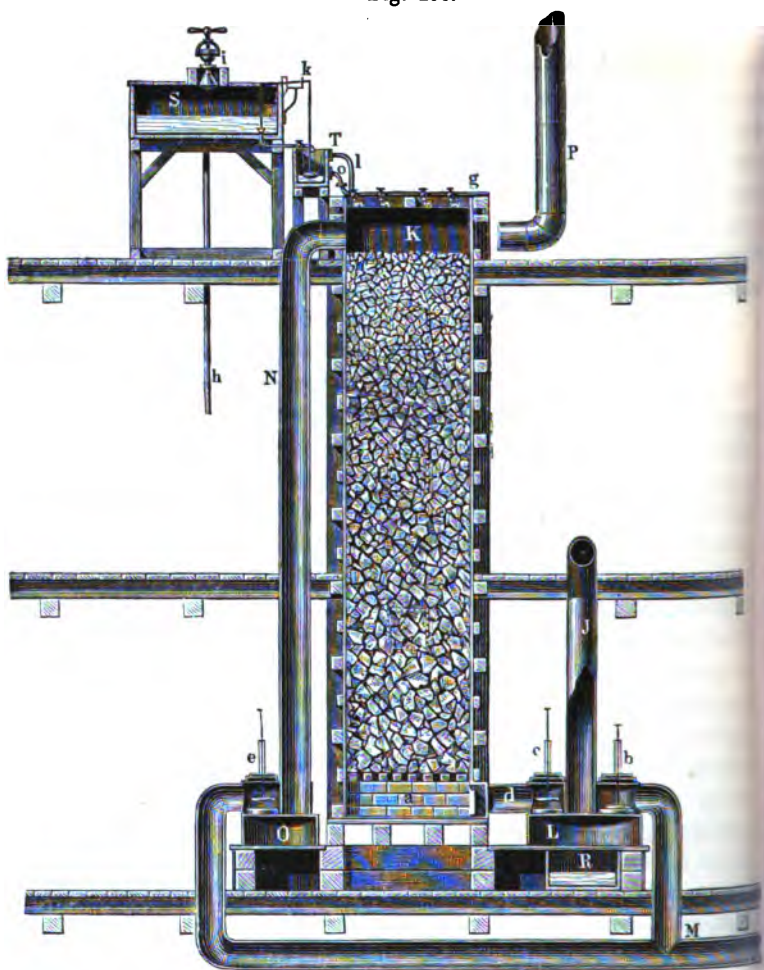
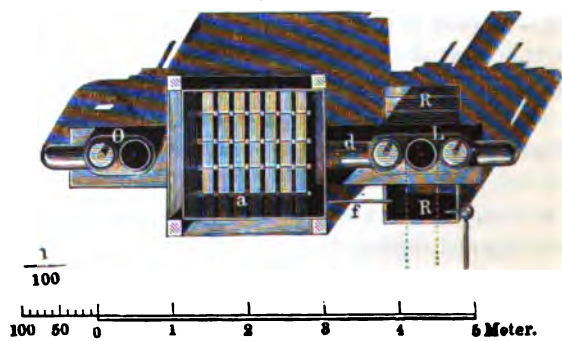


Fig. 196.



tingly prefer it even in such cases where it would be possible to draught the chambers direct from the top of the Gay-Lussac tower (p. 427); if for no other reason, because in this case the exit-"sight" can be placed on the ground-level, and is thus far more frequently observed by the manager than where he has to go up to the top of the tower for looking at it. But apart from this, the regulation of the draught is much easier with a chimney than without it.

Distribution of the Feeding-acid.

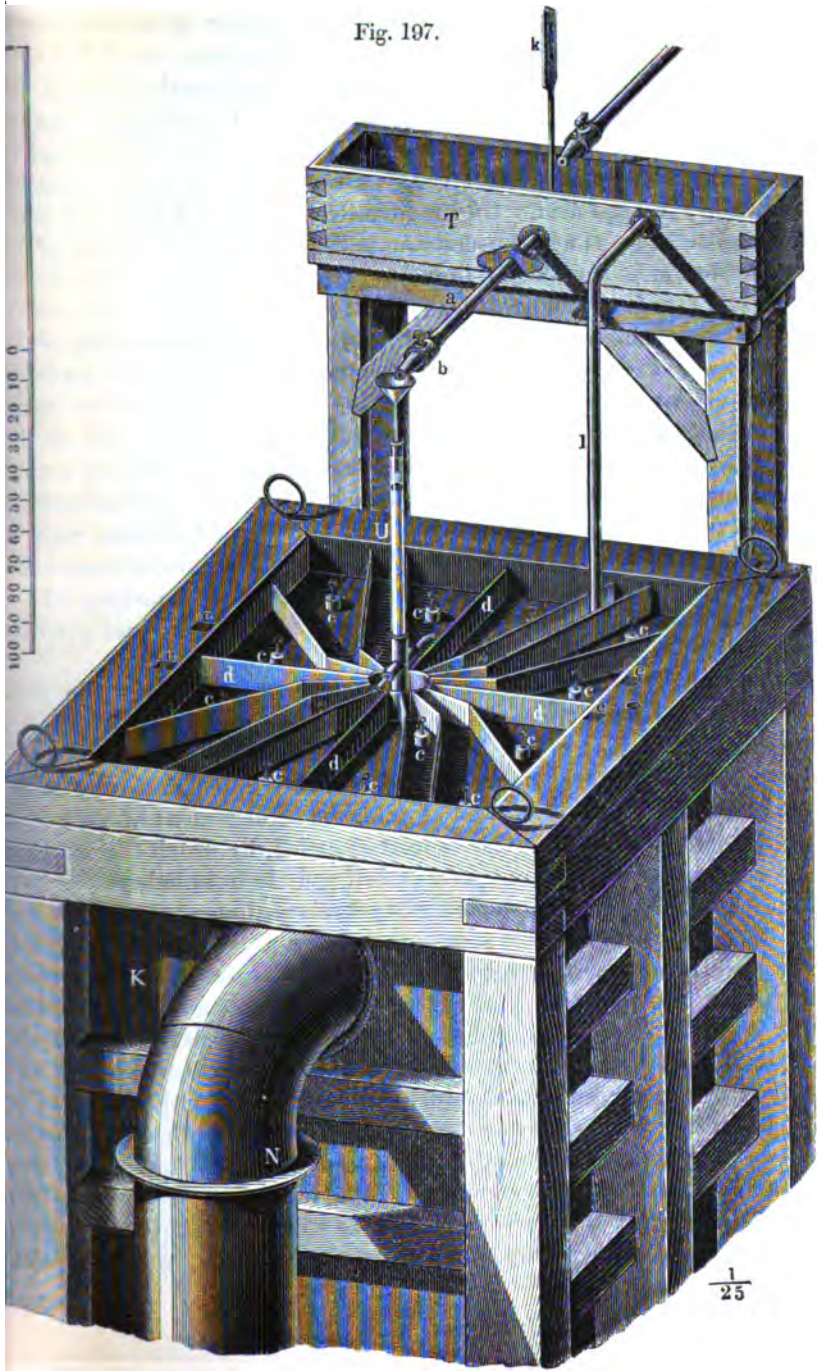
In this process it is of great importance that the supply of sulphuric acid, which is to deprive the gases of their nitrous acid, be exactly regulated, and that from the beginning this acid be spread equally over the coke; otherwise too much sulphuric acid may be used, and the gas may pass through the tower without giving up the whole of its nitrous acid. Special care must therefore be taken in the construction of the apparatus for spreading the acid. In the Freiberg towers this apparatus consists of two leaden tanks, S and T (fig. 195), and the special distributing arrangement fixed on the cover *g*. The acid is generally charged into the larger tank S from the lower part of the works by means of a pumping-apparatus, consisting of an air-tight vessel, into which air can be forced by means of a pump, which then forces the acid upwards through a pipe, *h*, reaching to the bottom of the vessel. This pumping-apparatus will be described in detail below. The pipe *h* ends at the tank S in a rose, *i*, made of "regulus" metal (a mixture of 5 parts of lead and 1 part of antimony); this rose serves for retaining any solid bodies suspended in the acid, and can be opened at the top in order to be cleaned. From the tank S the acid runs through a tube at its bottom into the smaller tank T; the supply into the latter is regulated automatically by means of a lead float suspended from an arm of the beam *k*, which in descending lifts a conical valve suspended from the other arm, that closes the running-off tube when the float rises too high. The tube *l* only serves for taking away any excess of acid in case of an irregular working of the float, so as to avoid any running over.

From the smaller tank, T, the acid runs to the tower K, where it has first to pass through the spreading-apparatus. An ordinary oscillating bucket was formerly used as such; but the

quantity of acid employed is so small that the oscillations only took place at pretty long intervals, and too large a quantity of acid was then emptied out at a time; moreover the play of the bucket was often interfered with from mechanical causes. At most works, therefore, it is no longer used. Another arrangement (sketched in fig. 195) consists of four series of four dropping-tubes each, fixed in the top of the tower at equal distances; they are provided with a funnel at the top and a swan-neck bend at the bottom, inside the tower, so as to form a lute against the outside air by the liquid remaining in the bend. The acid is conveyed to these drop-tubes by the tube *o*, which divides itself into two arms, running each between two rows of the drop-tubes, and provided with a small tap for each of the latter, so that each small tube gets its special supply of acid. There are thus sixteen taps for the regulation of the flow of acid. This is a very faulty arrangement; for it is next to impossible to regulate them all so as to give a perfectly equal supply from each, considering the very small quantity of acid that has to pass through them; and both the taps themselves and the bends of the tubes are also very easily choked up.

For this reason another arrangement for distributing the acid, which was first applied at the Aussig chemical works by Mr. Schaffner, has been for many years generally preferred, namely the *acid-wheel*. In this the supply of acid is regulated by a single tap, which can be opened wide enough so as not to be so easily choked as the sixteen small taps in the former arrangement. Fig. 197 represents this apparatus on a scale of 1:25. In the top of the tower there are sixteen holes, *c*, through which the acid trickles on to the coke below. Each hole has an upstanding rim about $1\frac{1}{4}$ inch in height, which is covered by a lead cap, nicked at the bottom in a few places to the depth of $\frac{3}{4}$ inch, so that the acid can pass through without hindrance. As soon as the top of the tower is covered with acid to the depth of that rim, the acid runs over into the inside of the tower; but no gas can escape through the holes, since they are luted with acid. The spreading of the acid is effected by a small reaction-wheel U, fed from the tank T by the tube *a* and the tap *b*, which regulates the supply. The lower part of the wheel and the two arms consist of lead; in this is fixed above a strong glass tube, and below another short glass tube, drawn out to a point which runs in a socket of glass or lead. One of the arms is also fitted with a glass tube, from which the acid runs out. There is a

Fig. 197.



guide, consisting of two parallel rods of lead or of wood covered with lead, which rest on frames fixed in the holes *e e* of the top-frame, and on which four glass tubes are placed close to the upright column of the apparatus, so that they form a square within which the column revolves. As soon as the column is filled with acid, the wheel revolves regularly, the liquid running out of the open arm. On the quantity of the acid run in depends the height to which the column is filled and the velocity of its revolution. The axle of the wheel is exactly in the centre of the tower; and a cylinder of lead about 4 inches in height is burnt to the top of the tower, so as to prevent the acid from getting to the centre. From this cylinder sixteen radial ledges *d*, also made of lead and burnt to the top-lead of the tower, branch off at equal distances. These are continued in a straight line as far as the periphery of an imaginary circle, beyond which the wheel cannot pour out any acid, and then alter their direction; so that between each two of them one of the above-mentioned sixteen holes is placed. Thus the top of the tower is divided into sixteen compartments, each of which contains an opening for running off the acid, and all of which are fed by the wheel with an equal quantity of acid.

In England the spreading-apparatus was generally made altogether of lead; we shall, further on, give a drawing of such a spreading-wheel in the description of the Glover tower.

Since it happens now and then that the reaction-tube stops, especially with a small feed of acid, the arrangement of Seybel, at Liesing near Vienna, can be recommended, by which the wheel at each revolution strikes against a bell audible from below.

Even the best-constructed acid-wheels are liable to being stopped now and then, and this sometimes gives a great deal of trouble if it is not at once perceived, as the tower ceases to work properly and much nitre gets lost. Hence a new system has been pretty generally introduced, which works quite as well as the acid-wheels, without a mechanical movement liable to get disturbed. It consists in running the acid into a vessel provided with a number of *overflows* kept exactly at the same level, each of these communicating with a separate pipe which leads the acid into the tower. This system can be carried out in a variety of ways, one of the best of which is shown in fig. 198, as seen from above, fig. 199 in transverse section, fig. 200 in perspective view, with the sides

partly cut away. From the top *a* the liquid runs into the central vessel *A*. The cover *b* is not exactly necessary, but is best provided, and is made loose, so that the interior of *A* is easily accessible. The cylinder *A* is nicked at the bottom, so that it communicates

Fig. 198.

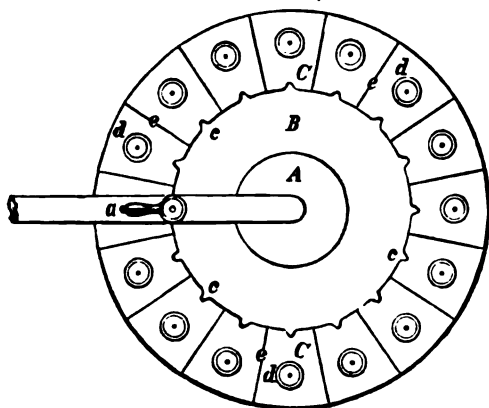
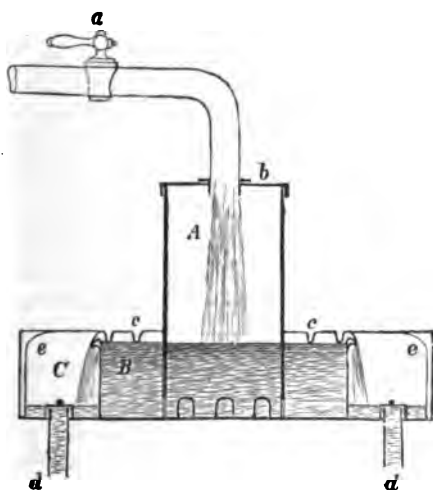
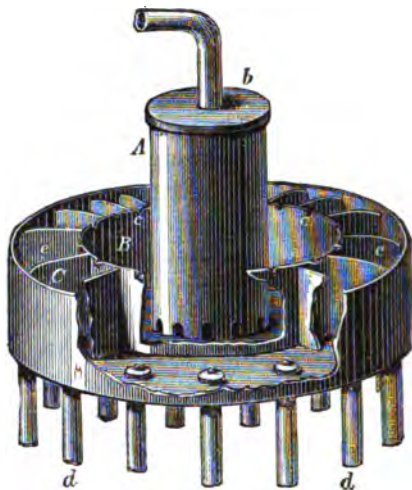


Fig. 199.



with the wider but lower trough *B*. This is provided all round its circumference with overflow-lips (*c, c*), which may be close to one another ; sometimes 30 or 40 of these are made. They must be

Fig. 200.



arranged in such manner that when B is once filled, all the overflows, *c, c*, function in the same manner; this can be easily attained by dressing the lead of the lips a little up or down, as the case may be. Once right, they act always in the same manner. The trough B is surrounded by the wider trough C, which is divided into as many cells as there are lips in B. Each cell is independent of its neighbour; but the partitions, *c, c*, are cut out on the top, so that, in case of the pipe of any one cell getting stopped up, the liquid overflows into the next cells. Each cell is also provided with a separate pipe *d*, made tight in its bottom, and hydraulically sealed either there, as it is shown in the diagram, or else on or within the tower. The whole is generally, with Gay-Lussac towers always, made of lead, but it can also be made of earthenware, iron, or other material suitable for any special case.

Briegleb (G. P. 10,386) has constructed a distributing-apparatus consisting of a cone made of regulus metal, on the top of which a jet of acid is directed. The upper part of the surface of the cone is plain, but the lower part is fluted, so that the acid is distributed into a number of jets which are caught in a circular vessel surrounding the base of the cone, and are separately carried away by pipes. No doubt this apparatus can be made to work properly, but it is much less easily kept in order than the simple overflow apparatus shown on p. 527.

A very ingenious, but somewhat complicated distributing-apparatus, in which a mechanical revolving drum is employed, is described in the patent of Brock and Saye (No. 11,492 of 1885, J. Soc. Chem. Ind. 1886, p. 487).

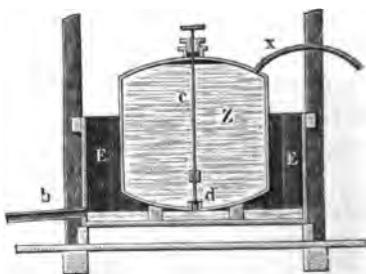
It is a matter of course that the working of a column (whether it be a Gay-Lussac, or a Glover tower, or a hydrochloric-acid condenser, &c.) is all the more efficient the more uniformly the feeding-acid is distributed over its whole area. It is equally self-evident that towers of a large horizontal section require more feeding-places than narrow ones. It may be laid down as a general rule that there ought to be no smaller number of distributing-pipes than one to each superficial foot of the cover of the tower; but this is a minimum which is greatly, and no doubt advantageously, exceeded at many works.

The *regularity of the supply of acid* to the coke-tower is of the utmost importance for its good working. The whole acid-chamber process is so constituted that its course must be kept as continuous and uniform as possible, and the large bulk of the lead chambers in this case serves as a regulator, similar to the air-vessel of a blowing-engine, so that the gas, on leaving the chamber, issues, or at least ought to issue, with nearly absolutely uniform speed and composition. In similar spaces of time there will therefore be a similar quantity of nitre-gas leaving the chambers; and this in the absorbing-tower should always find the same quantity of acid, lest either there be an escape of nitre-gas or the nitrous vitriol come out too weak. But if the acid flows out of a tank, the opening of the tap remaining the same, the flow will be much quicker at the beginning, when the tank is full, then afterwards, when it is partly empty, and the tower will thus be fed very irregularly. The speed of outflow of liquids decreases in the proportion of the square roots of the heights of liquid in the tank; for instance, when the tank is filled to the height of 4 feet, the flow of acid will be twice as fast as when it only stands 1 foot high—both being cases which often happen in practice.

In order to secure a very regular supply of absorbing-acid to the tower, several arrangements have been adopted, apart from that described above—for instance, Mariotte's vessel (page 405) or the apparatus shown in fig. 201. The vessel Z is placed with its mouth downwards in an open basin E, in such a manner

that its mouth is luted by the vitriol contained in the basin; therefore nothing can run out of Z. But as the vitriol runs away from E through the pipe *b* on to the coke-tower, the

Fig. 201.

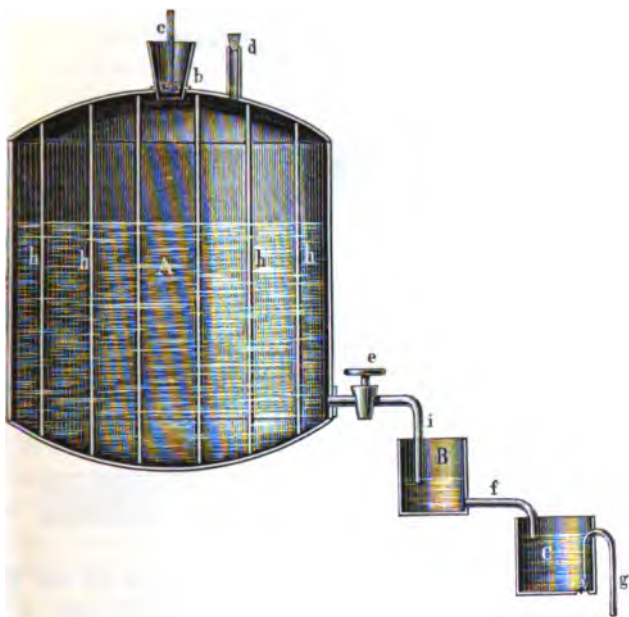


level of E is lowered, the mouth of Z becomes free, a few air-bubbles enter, and acid flows out till the original level is reached, and the mouth of Z is luted again. The valve *d*, with the valve-rod *c* passing through a stuffing-box, serve for closing the mouth of Z during the time that this vessel is being fed through *x*.

In a simpler shape the same principle used to be applied some years ago in a few English alkali-works, as shown in fig. 202. A is a pretty large leaden vessel, protected against collapsing by iron rods covered with lead, connecting its top and bottom; these are required because the air in A is at a lower pressure than that outside, from which those vessels used to be called *vacuum-retorts*. They are filled through the funnel *b*, the air escaping through *d*; *b* is then closed tightly by the valve *c*, and *d* by a stopper. From the cock *e*, made of antimony and lead, which must close air-tight, proceeds a pipe *i*, which enters and descends about halfway to the bottom of the small vessel B. The latter has, at the bottom, an exit-tube, *f*, whose bore is a little smaller than that of *e*. When the cock *e* is opened, acid will run out and air will enter into A at the same time; but as the acid cannot run out of *f* as fast as it runs in, its level will rise in B, and as soon as it closes the mouth of *i*, no more acid can run out of A, because no air can enter; but as soon as a little acid runs out of *f*, a few air-bubbles will get into A, and a corresponding quantity of acid will run out; so that the level of the acid in B will remain nearly the

same until A is totally emptied. The acid, therefore, runs out of *f* constantly under that pressure which is determined by the vertical distance between the mouth of *i* and the junction of *f*—

Fig. 202.



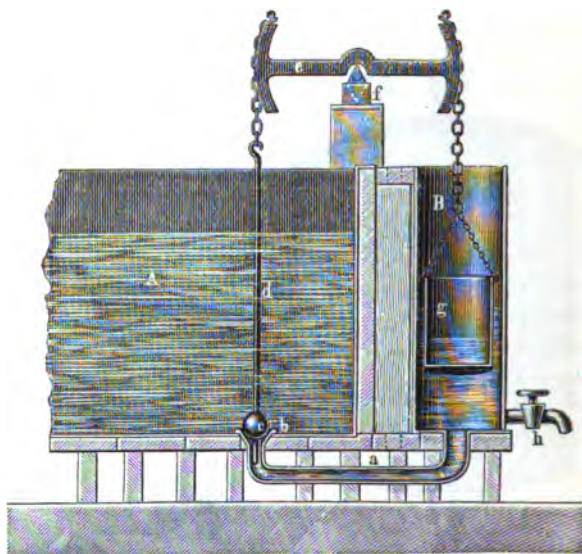
that is, in a uniform jet. It thus gets into the vessel C, and from this through the intermittent siphon *g* into the coke-tower.

The vacuum-retorts have been abandoned again, because their action entirely depends upon no air entering the vessel A otherwise than through the cock *e*; in any other case the vessel B must run over, and the action of the apparatus as a regulator ceases altogether. It is, however, very difficult always to make a *perfectly* air-tight stopping at *b* and *d*; and therefore overflowing often happened. Besides, in consequence of the partial vacuum in A, air was apt to enter through the least fault in soldering the lead &c.

The object in question is better accomplished by the *balancing apparatus* shortly described above; it shall now be explained in

more detail. In fig. 203, A is the large acid-tank on the top of the coke-tower, made of wood lined with lead, which is filled from time to time. Beside it stands a lead cylinder B of equal

Fig. 203.



height and 12 inches wide; the two communicate at the bottom through the lead pipe *a*. This pipe ends in A with a valve-seat *b* of hard lead, bored out in a taper shape. In this plays a ball-valve *c*, also made of hard lead ("regulus"), which is continued below into a small guide-rod, and above into the lead-covered iron rod *d*, which projects above A, and is suspended by a short chain from one arm of the balancing-beam *e*. The latter swings with its centre on a steel edge *f*, and carries on its other arm, exactly over the cylinder B, another chain, from which a leaden bucket *g* is suspended inside B. Acid is poured into the bucket *g* until it sinks to a certain depth in the acid standing in B; by pouring in more or taking out some of the acid in *g* that depth, and with it the height of acid in B itself, can be regulated at any time: this bucket is therefore a form of float, preferable to the solid lead float figured by Schwarzenberg. The bucket *g* is so weighted, and the length of the chain such, that at

a certain height of acid in B the valve *c* must close the opening *b*. The valve *c* with the rod *d* and its chain is about as heavy as the float *g* along with its chain, and closes the opening *b* so long as a portion of the weight of *g* is neutralized by the upward pressure of the acid in B. As soon, however, as the cock *h* begins to run and the float sinks down, the rod *d* is raised by means of the beam *e*, and the ball-valve *c* leaves the opening *b* free; thus acid flows across into B through *a*, lifts the float *g*, and *c* sinks down into its position, closing *b* again. Thus, by small oscillations of *e*, always the same quantity of acid will run out of B in the same time, as this only depends on the weight of *g* and the length of the chain, but is independent of the level of the acid in A. The ends of the beam *e* are shaped as segments of a circle, in order (by means of the chains) to convert their circular movement into a rectilinear one for the rod *d* and the bucket *g*.

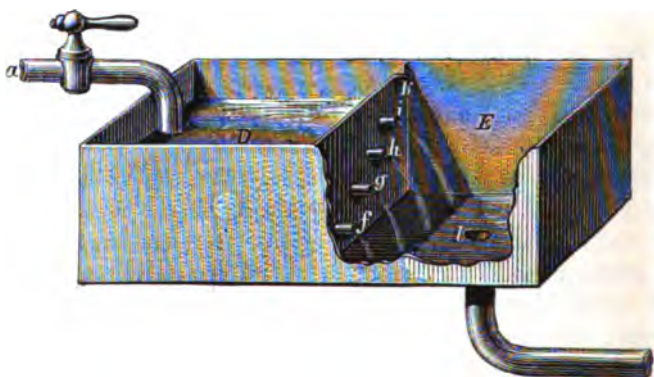
The above apparatus, as it has formerly been figured in books and carried out in many works, does not work well, and has even been given up in many places where it had been erected. In the first place, the beam is usually represented swinging on a pin which passes through its centre; but then the friction is very great, and soon becomes greater by the iron rusting, so that the beam sticks fast. This cannot happen if the arrangement is that shown in the above diagram, viz. a steel edge like those of delicate balances; when strongly plated with nickel it remains free from rust. But, above all, the valve *c* ought not to be a truncated cone, as it is generally represented, but it should be ball-shaped. The guiding by the arc-shaped arms of the beam is not so absolutely vertical that a conical valve cannot now and then jam itself in its seat during its play upwards or downwards; in that case the apparatus ceases to work. If, however, the valve is ball-shaped, a slight deviation from the vertical does no harm, as it always closes the hole, and jamming fast is out of the question. Whilst those manufacturers who had erected the above-mentioned imperfect apparatus were mostly induced to give it up again on account of its constantly breaking down, the arrangement figured here works with the greatest ease and regularity and can be highly recommended. At some of the largest works, from not being acquainted with the *right* way of making the apparatus, they have abandoned automatic regulation altogether, and leave it to the workmen to set the running-off tap

of the acid-tanks according to the level of the acid—a very rude method, which, according to the explanation just given, there is no reason for retaining.

(Whenever “lead-covered” iron rods are mentioned, it should be understood that for this purpose the iron rod is put into a pressed lead tube of convenient bore, and both ends of the latter are soldered up.)

Some works employ for regulating the rate of feeding the contrivance shown in fig. 204, which is interposed between tap *a* and the central vessel A in the apparatus, fig. 199. The liquid runs

Fig. 204.



from *a* into a leaden box, divided into two compartments, D and E. D communicates with E by the four pipes *f*, *g*, *h*, *i*, placed at different levels, and the lip *k*; E is at the bottom provided with a wide outlet tube *l*. According to the width to which tap *a* is opened, box D will be more or less filled; with the strongest feed the acid will run into compartment E out of all four pipes and the lip *k*; with a smaller feed fewer of the pipes will come into action. Supposing the attendant to be instructed to work with three pipes, he will have to see that the acid runs only out of *f*, *g*, and *h*, the pressure being almost constant at the level of *h*. This, of course, is greatly preferable to regulating the position of tap *a* by mere rule of thumb, and it operates independently of the level of acid in the main reservoir to which tap *a* belongs. This contrivance acts very well.

Pumping-Apparatus for Acid.

It will rarely be possible to feed the acid-tank on the top of the absorbing-tower with concentrated vitriol by natural fall ; where the concentration takes place in the Glover tower, that possibility is excluded from the outset. There is therefore need for an *apparatus to force the acid up to the top of the absorbing-tower* ; the same apparatus will also serve for forcing the nitrous vitriol and the chamber-acid to the top of the denitrating-tower. Ordinary force-pumps cannot be employed here, because these cannot be made without using metals which are acted upon by the acids, at least not for such quantities as have to be treated in this case. Fortunately we have two metals which resist the vitriol very well, viz. cast iron and lead, and with the aid of these an apparatus can be constructed in which the force-pump acts only indirectly, viz. through the compression of a column of air, which thus enters into the forcing-apparatus proper, and conveys the acid to any desired height. A similar principle has been employed long since in sugar-works, where there is an equally good reason for avoiding direct pumping, viz. that such pumps cannot be kept quite clean, and would spoil the sugar-liquors by the acids generated in them. The liquids are therefore pumped up by running them into a small upright steam-boiler, from whose bottom a delivery-pipe rises upwards, and by admitting steam at the top, whose pressure forces the liquid upwards in the delivery-pipe until the apparatus is quite emptied. As the liquids in sugar-works are mostly treated at a boiling heat, they are not excessively diluted by condensed steam.

In sulphuric-acid works it would not do to proceed precisely in the same way ; for the strong acid would instantly condense the entering steam, and thus there would not only be no pressure upon it, but it would actually have a sucking action, and it would at the same time become very much diluted and very warm, and therefore useless for absorbing the nitrous gas. It has certainly been suggested (see Kerl-Stohmann's *Chemie*, 3rd ed. vi. p. 239) to connect the pressure-apparatus with another boiler, and to admit steam into the latter ; it would then cause a sudden expansion of air in the second boiler, and this would press on the surface of the acid in the first boiler and force it up in the delivery-pipe. If such an arrange-

ment has really been introduced into practice, it must, for all that, be very little adapted to the purpose; there will be incomparably more steam used in this way than suffices for working an air-pump, and a portion of the steam will certainly pass over into the pressure-apparatus and dilute the acid within it.

The ordinary plan of working (introduced about 1838 by Harrison Blair, according to Richardson and Watts's 'Chemical Technology,' vol. i. pt. v. p. 217) is this, to convey air compressed by an air-pump or, more properly speaking, by a small blowing-engine into the pressure-apparatus, above the surface of the acid, exactly similar to the way in which every chemist in his wash-bottle forces the liquid up in the outlet-tube by blowing air in through another tube. In this there is no special limit of height, so long as the apparatus is made strong enough to resist the pressure and the air-pump is sufficiently powerful.

The air-pumps are generally constructed in this way:—The steam-cylinder and the air-cylinder are both fixed on a common horizontal ground-plate, or cast in one piece with the same; they are then worked by a common piston-rod with a piston at each end. A cross-head sliding between motion-bars gives the necessary guidance; and a pretty heavy fly-wheel secures regular action. The dimensions of the pump are chosen according to the size of the works; for a set of chambers of from 140,000 to 200,000 cubic feet a steam-cylinder of 8 inches diameter, an air-cylinder of 12 inches diameter, and a stroke of 18 inches, with from 40 to 60 revolutions per minute, suffice for pumping all the nitrous vitriol, concentrated acid, and chamber-acid. The compressed-air pipe in this case has $1\frac{1}{4}$ to $1\frac{1}{2}$ inch bore. Much care has to be taken of the valves of these pumps: if they work with too much noise, they last only a very short time; but, in any case, a second pair must always be ready for putting on when the first give way. At the works formerly managed by myself, I sent the exhaust-steam of the engine into the steam-pipe for the chambers, the steam-boiler belonging to which worked at only 10 lb. pressure per square inch; thus the steam for pumping the acid was got for next to nothing, since only the difference of pressure before and behind the steam-cylinder had to be made good by consumption of fuel. (This description was given in the first edition of this work (1879), and is therefore much prior to the very similar proposal of Sprengel, B. P. No. 10,798, of 1886.)

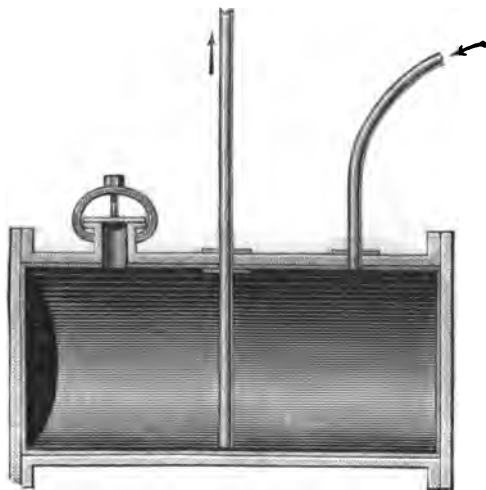
The air-pipe, which must be made of very strong lead tubing, is not conducted direct from the air-pump to the pressure-apparatus, because in that case acid would inevitably be squirted back into the air-cylinder and soon ruin the valves; but the air-pipe is carried upwards a distance of from 10 to 13 feet, and then as much downwards, before entering the acid-vessel. Close to the air-cylinder a small branch tube with a cock is soldered on, in order to let out the air when the pumping is finished. Sometimes there is also a pressure-gauge fixed to it: but this is not of much use; for, in the first place, it is soon destroyed by the violent oscillations at every stroke of the piston and by the acid fumes; and, secondly, the workman can judge much more conveniently than by looking at the gauge, from the noise of the pump and the valves, whether it works easily or heavy—that is to say, with much or little pressure.

The acid-vessel serving as pressure-apparatus is made in various forms. At the commencement (and even now in many places) it

Fig. 205.



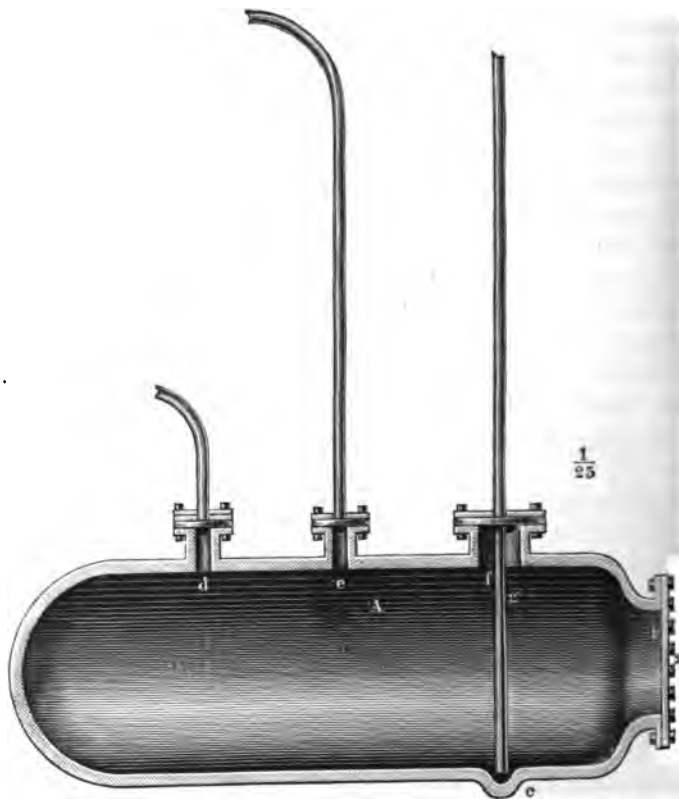
Fig. 206.



was made in the shape of a soda-water bottle, as shown in fig. 205, afterwards as a horizontal cylinder (fig. 206) with bolted-on covers; but it is now more usually, as shown in fig. 207, a horizontal cylinder

with one semicircular and one neck-shaped end, the latter closed by a man-hole door. These vessels are called "acid-eggs." The vessels like fig. 206 are usually lined with lead; those like figs. 206 and 207 are not. In England experience has everywhere shown that it is needless to protect the cast-iron of the acid-egg by a lining of lead; even the nitrous vitriol and the chamber-acid act so little on cast iron that such a protection becomes unnecessary.

Fig. 207.



have found an acid-egg, after five years' continuous use for all three kinds of acid, in entirely good working-order. Lining with lead has this drawback, that as soon as a little air enters between the lead and the cast iron by the smallest possible crack

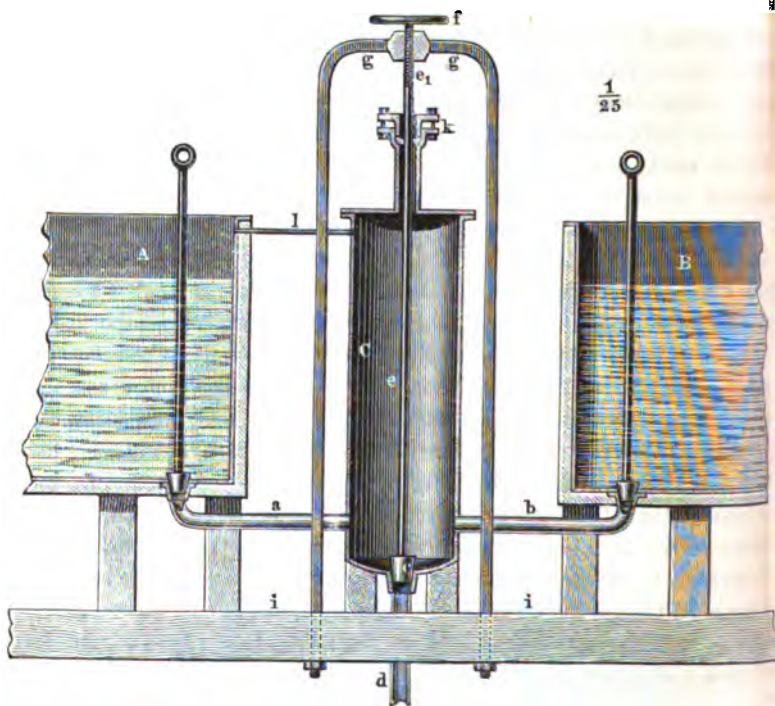
the lead is driven away from the iron in many places, and its protecting action becomes quite illusory, whilst the contents of the egg are diminished.

The horizontal has the advantages over the vertical shape:—first, that no well is needed for the acid-egg, which may lie on the floor and thus be accessible all round; secondly, that in the case of excessive pressure, the weakest part (viz. the man-hole) being situated sideways, the acid squirting out is not so likely to do damage to men and machinery as in the case of squirting out vertically, especially if the cylinder is at once laid with the man-hole turned away from the machinery.

In fig. 207, A is the acid-egg, whose walls are 2 inches thick; B is the neck, with the man-lid *a* fixed to it by bolts and nuts; a thick india-rubber washer makes the joint tight; *c* is a recess at the bottom of A, into which the delivery-pipe *g* projects, in order to expel the contents of A as completely as possible; *d*, *e*, and *f* are three branch pipes, *d* for introducing the acid, *e* for the air-pipe, and *f* (the widest of them) for the delivery-pipe. The pipes have each a strong lead flange soldered to it, which rest on the flanges of the branches *d*, *e*, *f*; by putting loose iron washers on the top, and screwing all three together by bolts and nuts, the joint becomes perfectly tight. The inlet branch *d* may be left open and closed after each filling by a small plate bolted on; but in most cases there is an *inlet valve* for the acid, of the shape shown in fig. 208. (The plain stoppers with lever-rods, figured in Muspratt's 'Chemistry,' cannot support any great pressure.) A and B are acid-tanks, which need not be placed so close to the pressure-valve C as they are represented in the diagram. C is a cylinder of strong lead, about 10 inches wide, whose top is at a level with the top of the tanks, but which is deeper than these, so that they may communicate with C through the pipes *a* and *b*, connected with their bottoms. *a* and *b* end in the bottoms of the tanks with valve-seats of "regulus" metal, and are usually closed by taper valves with long lead-covered handles: there is no pressure upon these exercised from below; and therefore they need not be provided with any special contrivance against this. When it is necessary to run the contents of these two tanks, or that of a third tank, not visible in the diagram, but similarly communicating with C, into the acid-egg, the respective bottom-stopper is taken out, the bottom-valve *c* in C also remaining open. The latter valve, which

must be very well ground into its regulus seat, communicates through the pipe *d* with the corresponding inlet branch of the acid-egg. On the top it is connected with the lead-covered iron rod *e*, which ends above in a screw-worm *e*₁, and can be turned by means of the hand-wheel *f*. A very strong iron frame, *g g*, with

Fig. 208.



a female thread corresponding to the worm *e*₁, is bolted to the bottom-joists, *i i*; both the timber and the iron rods must be very strong, as there is a good deal of strain upon them in screwing the valve in and out. As the cylinder *C* is equal in height to *A* and *B*, it can never run over; and when the acid in *C* stands at the same level as that in the tank, the valve *c* is screwed down tightly by means of the hand-wheel, the corresponding stopper is put into its seat in the tank, and the air-pump is started. The whole pressure of the acid, which has sometimes to be lifted to a height

of 100 feet, will then act from below on the valve *c*; and unless the latter has been screwed down perfectly tight, the acid will squirt out vehemently. Although, with a little care on the part of the workman, this should never happen, yet several accidents caused by men being splashed with acid have led to providing the cylinder with a cover and a stuffing-box, *k*, through which the rod *e* passes; the splashing does then no harm, as the acid cannot get out. At the same time the stuffing-box serves as a guide for the valve-rod, which would otherwise have to be provided in some other way. Sometimes (not always) there is a small pipe provided for taking any acid squirted out into one of the three tanks. In this way the same acid-egg can serve for pumping strong acid, nitrous vitriol, and chamber-acid out of their respective tanks one after another.

A self-acting apparatus for filling the acid-eggs, constructed by Mr. Harrison Blair, which, Mr. Mactear says (*Journ. Soc. Arts*, 1878, p. 558), works well, is shown here according to the description in Richardson and Watts's

Fig. 209.

'*Chemical Technology*,' vol. i. part v. p. 217. A (fig. 209) is a strong cylinder of lead closed at both ends [probably cast iron would be preferable]; B a



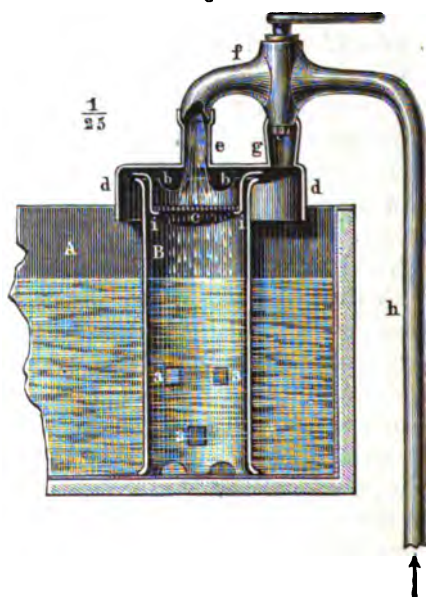
valve-box, and C a delivery-pipe, into which the pipe D enters a little above the vessel. D is continued to E, where it passes to the inside of the vessel, and F joins D at the lowest part. G is the pipe which brings the air from the pump. So long as D contains no liquid, the air from the vessel will pass through, and by thus preventing any pressure on the liquid in the vessel, it will be filled through the valve-box. When the vessel is full, the egress of the air through F being stopped by the liquid, the latter will be forced up E (being lower than F), which, acting as a siphon, fills D and effectually stops the passage of air. As the pressure of air increases, the liquid rises up the delivery-pipe and is conveyed to any required point, while the liquid in D falls with the level of that in the vessel, until this sinks below the bend in D, when the air rushes through, carrying with it all the liquid out of D. This leaves a free passage for the escape of air during the time the vessel is again being filled, the air-pump working the whole of the time.

At the Rhenania works the rod *e* of the inlet valve *c* (fig. 208)

is coupled with the air-cock on the acid-egg in such manner that when the egg is full the attendant cannot by mistake shut the air-cock first, but he is obliged to screw down the valve *c* before he can shut the air-cock and open the connection with the air-pump.

As soon as, in the ordinary kind of apparatus, the pumping is finished, the air-pump, to which now no resistance is offered, begins all at once to go extremely fast, and draws by its noise the attention of the workman to the necessity of stopping it. Directly after, the air-cock in the pipe conducting the compressed air to the acid-egg is opened. Nevertheless some compressed air accompanies the last portions of the acid and rushes vehemently out of the top of the delivery-pipe; and in order to *prevent the acid from splashing about* a special contrivance must be adopted, for instance that shown in fig. 210. A leaden cylinder, open at top

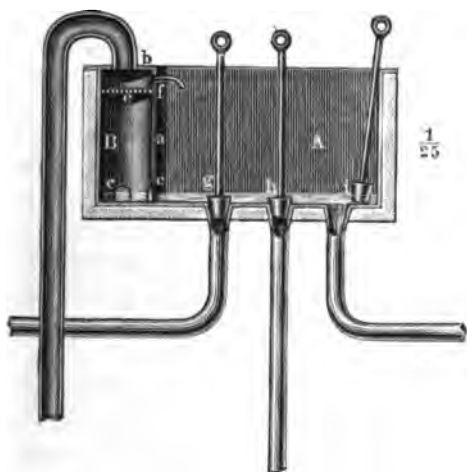
Fig. 210.



and bottom, stands within the tank A; it is jagged out at the bottom in a few places; and the holes *aa* higher up also help to give free communication between B and A. Also the top of B is

it out pretty deeply in a few places (*bb*). Within B the perforated plate *c* is suspended by a few lead strips, *ii*; the whole is covered by a loose cover *dd*, which is kept at a little distance from the top of B by the lead strips, so that the air can escape between them. *d* has a flange of 8 in. depth; in the centre it carries a short tube *e*, to which the "regulus" cock of the delivery-pipe *h* is burnt. Since it is extremely difficult to keep such a cock tight, especially under great pressure, it is surrounded below by the pipe *g*, which also joins into *d*, and thus carries away the droppings. This contrivance acts in the following way:—When the acid forced up through *h* arrives at the top, it runs through *f* and *e*, then through the sieve *c* and into the cylinder B, whence it easily passes through into A. But in the last stage, when compressed air arrives at the same time with the acid, the latter cannot

Fig. 211.



be squirted about, nor can the current of air act upon the surface of the acid within the tank so as to splash it about; for it is broken by the sieve *c* and escapes through the openings of *c* and the annular space below *d* without doing any damage; the acid accompanying it runs quickly down through the sieve *c*. The cock *f* and the pipe *g* are required only when a single acid-egg has to feed several tanks placed at a considerable distance from each other, for instance one on the absorbing-tower and two on the Glover tower;

for then the delivery-pipe must be divided into two parts, and each must be provided with a stop-cock, only that leading to the working tank being opened. If, however, the tanks to be filled are placed close together, no cocks are required, but the simpler arrangement, fig. 211, can be employed, which can also be made much smaller than (for the sake of clearness) it has been drawn here. Within the same lead-lined box A there is a special compartment B constructed by means of a lead partition, *a*, and cover, *b*. The side of B is jagged out at the bottom at *c c*, in order to communicate with A. The delivery-pipe joins into the cover *b*; the air rushes against the sieve *e* and escapes out of the pipe *f* without doing any harm. In the bottom of A there are three valve-seats, *g*, *h*, and *i*, connected with as many pipes leading to different tanks; but only one of the valves is left open at a time; the two others are closed by plugs, and the tanks communicating with them therefore receive nothing.

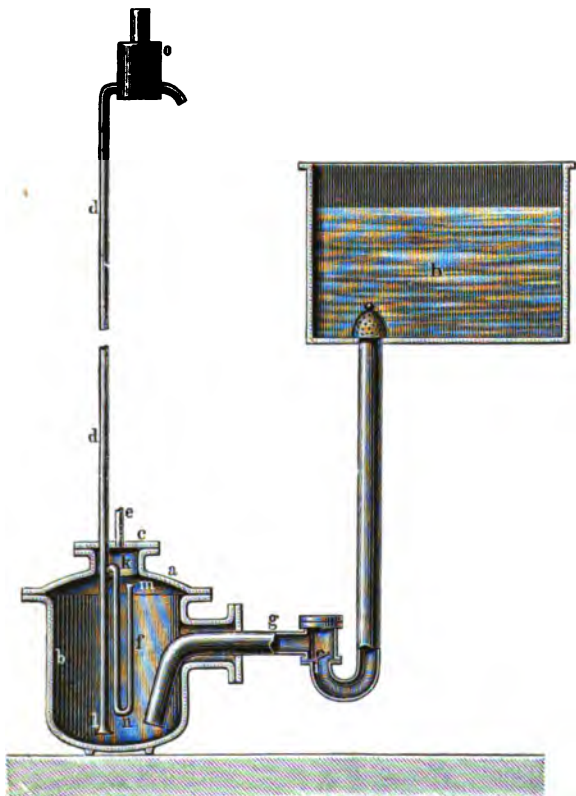
In smaller works there is usually only one acid-egg, which serves for pumping all the strong acid, nitrous vitrol, and chamber-acid, one after another. In this case the air-pump has nothing to do during the time that the egg is getting filled from one of the tanks; but if the cubic contents of the chambers do not exceed 200,000 cub. feet, there is time enough for that. But where the chamber-space is larger, there will be at least two acid-eggs required, of which one usually serves for the strong acid and nitrous vitriol, the other for the chamber-acid; in that case the same air-pump can do all the work if the air-delivery pipe is provided with two branches and two stop-cocks, one of the eggs always getting filled whilst the contents of the other egg are being pumped up; the air-pump is thus fully utilized.

Johnson and Hutchinson (E. P. 8141, of 1885) describe a combination of three upright vessels, so connected that the compressed air contained in one of them is always utilized in the next, and is not lost as in the usual process.

A somewhat different kind of acid-lifting apparatus is Laurent's pulsometer, which is certainly much more useful for hydrochloric or nitric acid than for sulphuric acid; but as for the latter also great advantages are claimed for this apparatus, we shall describe it here, as seen in figs. 212 to 214. It is made of cast iron for sulphuric acid; with lead pipes (figs. 212 and 213), and of stoneware for hydrochloric or nitric acid (fig. 214). In the former case the joint between the cover *a* and pan *b* is best made good by a lead washer,

in the latter case by an india-rubber washer; *c* is the man-hole, with the rising main, *d*, and the pipe *e* for compressed air. The rising-main *d* has a side connection with the swan-neck pipe *f*. The feed-pipe *g* is connected with the store-tank *h*; the latter must

Fig. 212.



be fixed at such a height that even when the pulsometer is quite full, and *h* nearly empty, there is still a greater head of liquid on the pulsometer than the length of pipe *f*. The clack *i* (which may be replaced by a ball-valve or by a Bunsen valve, as shown in fig. 214) prevents the acid from being driven back into *h* whilst rising in *d*. Pipe *d* must be fixed in such manner that it can be taken out together with pipe *f*, in order to look after the latter.

The play of the apparatus is as follows:—The acid runs from *h*

through *g* into *b*, during which time the air, continuously being forced in through *e* from the air-pump, escapes through *f* and *d*.

Fig. 213.



Fig. 214.



As soon as vessel *b* has been filled to the upper opening of *f*, the air cannot escape very well, and a little pressure ensues. In spite of this, through the momentum of inertia, the acid rises still a

little, arrives at the top of the siphon (at k), and causes this to act, whereupon the level of the liquid in all pipes becomes that of the outlet of f , that is m . As the air cannot escape now, the pressure gradually gets up and the liquid rises in pipe d , but sinks in vessel b . As the pressure on the surface of liquid in b must be the same at all points, and each point has also to bear the counter pressure of the column of liquid in d , the acid must sink exactly as much in the outer limb of f as in the vessel b , and the level must at last arrive at n . Now as the column of liquid between the lower end l of pipe d and the upper outflow at o is still rather higher than that from the lowest point n of the siphon to the outflow at o , the air must throw the acid from n out of o , the pressure within b must cease, and the vessel b must be filled again from h through i and g . Even if by an accident a little acid had run back from d into f and filled the siphon, this cannot prevent the filling of b from h , since this tank (as we have seen above) is placed high enough for this purpose.

If during the forcing up of the acid the outflow from o , owing to the friction in d , were not as great as corresponds to the volume of the air entering at b , strong pressure will ensue on the surface of liquid in b , and at last the acid in siphon f would be forced to point n , before the outer level in b had sunk to this point. Then the air will bubble up through n into d and out of o , and will keep the liquid column suspended. This bubbling can be perceived when putting the ear close to d , and can be remedied by closing the air-pump cock a little, and afterwards regulating the pressure in the following way:—In the air-pipe e , which is $\frac{1}{4}$ of an inch wide, a flanged joint is made between the cock (not shown here) and the cover c , in which a copper disk is placed, perforated with a pin-hole (say $\frac{1}{2}\frac{1}{4}$ inch). If with the cock quite open this hole is still too wide, so that the air in lieu of lifting the acid bubbles through d , the pin-hole is narrowed to the required extent so that in future the tap may be opened fully whenever the apparatus is to act. It can then go on for many years without any supervision, unless the valve i gets obstructed by impurities.

As during the time b is getting filled, the air escapes without any use, it is best to place the tank h at least five feet above b , and make pipe g very wide, so as to shorten the filling. The compressed air must be always under the same pressure, and the air-

can be cleaned in case of necessity by flushing the column with water, or even by taking out and washing them outside. In order to facilitate both the erection and the cleaning or dismantling of the column, the leaden shell is made in horizontal sections bolted together. All this is clearly shown in figs. 133 to 137 (p. 382 *et seq.*).

Working the Gay-Lussac Tower.

After the above explanations very little need be said on the working of the absorbing-tower. The following points have to be observed in this respect.

The *gas* entering the tower must show a distinctly red colour in the "sight;" on the other hand, the exit "sight," behind which a board painted white ought to be placed, should show a perfectly colourless gas. The gas escaping from the top of the tower, or of the chimney connected with it, ought not to produce red vapours when it meets the outer air. Furthermore the chamber-gas before entering the tower should be as *dry* and as *cool* as possible, lest the absorbing acid be diluted or heated. For this purpose the last chamber receives very little, sometimes even no steam, so that its acid remains at about 106° Tw.; moreover the gas is often conducted through a long pipe or a tunnel, or into a shallow box with several vertical partitions, where it has to go backwards and forwards. In these cooling-apparatus water may be applied outwardly to assist the cooling, especially in summer time. Sometimes the bottom of the box is covered with strong vitriol, in order to dry the gas; this, however, to a certain extent, only anticipates the tower. The *sulphuric acid* serving for absorption must show at least 144° Tw.; but this is only a minimum, which ought to be exceeded if possible; acid of 148° absorbs much better, that of 150° or 152° Tw. much better still; wherever possible, acid of 152° Tw. should be taken for the absorption. Such acid can be got without any difficulty from the Glover tower—with more difficulty from pans placed on the top of the pyrites-burners, where the acid rarely gets beyond 144°. Schwarzenberg even proposed to use acid of 170° Tw., because it absorbs three times as much as that of 144°; but this is out of the question, owing to the large additional cost of concentrating from 152° to 170°.

Above every thing care must be taken that the acid used for absorbing is as *cool* as possible. Hot acid absorbs very badly; much nitre is lost; and at the same time a weak nitrous vitriol is pro-

duced. Bornträger (Dingl. Journ. vol. cclviii. p. 230) goes so far as to demand cooling the acid down to 5°C ., but it is hardly possible to go to that length. In fact, at the French works they believe that 25° is the best working temperature. It is therefore necessary either to provide a very large tank for cooling the vitriol concentrated in pans or in the Glover tower before it is employed in the Gay-Lussac tower; or, as the cooling by mere exposure to the air is a very slow process, especially in summer, and in large works enormous tanks would be required for it, special cooling-apparatus is employed. As such many works use double spouts—an outer one filled with water, and an inner one, in which the hot acid runs. In this case it is rarely possible to apply the rational principle of running the cooling-water in a current opposite to that of the acid to be cooled, because, on account of the length of the spouts, there is no fall for this. Such double spouts also have a disagreeable tendency to swell out at the bottom whenever a little more pressure takes place, because the lead when hot loses part of its strength, which in any case is not considerable. This drawback can be avoided by the arrangement sketched in fig. 215, viz. by attaching to the spout, at about every 30 feet of its length, a tube rising perpendicularly from the double bottom through the upper spout and bending over the side of the latter; the water can issue out of this, in case of stronger pressure, without mixing with the acid. The upright tube also serves for the escape of the air-bubbles which are often contained in the water, and which may stop the stream as well as cause the spout to bulge out.

Fig. 216.



Among the various contrivances for cooling the strong acid, which, in spite of their great diversity, have nearly all one common feature, that of an extreme liability to break down, the following apparatus is at English works considered one of the most practicable. Fig. 216 shows a sectional elevation through the line AB of the plan; fig. 217, a section through CD; fig. 218, a sectional plan. The diagram is on a scale of 1:25; but the cooling-trough and its pipes, as a rule, must be longer than represented here (in order not to extend the diagram too much). For a weekly make of 100 tons of acid, for instance, the trough ought to be 20 feet long. It is 4 feet wide and 2 feet high, and lined with lead; two vertical lead partitions divide it into three compartments—two small ones, *a*, *b*, at the ends, and one large one, *c*, in the middle. *a* and *b* con-

tain acid, *c* water; *a* and *b* are connected by about 20 lead tubes, *d d*, of $1\frac{1}{4}$ -inch bore, which are burnt into the cross partitions and stay them at the same time, so that the partitions can easily resist the pressure of the liquids. The hot acid runs in through the pipe *e*, collects in the compartment *b*, and runs across to the com-

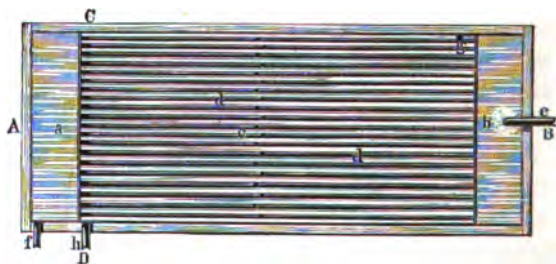
Fig. 216.



Fig. 217.



Fig. 218.

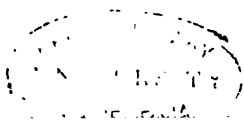


partment *a* through the pipes *d d*, in order to run away through the pipe *f*. Cold water runs into the inner box *c* through *g*; and the hot water leaves it again through *h*. The flow of acid through the great number of pipes is only slow; and the acid thus has time to give up its heat to the cooling-water. The vertical tubes, *i i* ($3\frac{1}{4}$ inches wide), attached one to each of the tubes *d d*, and projecting above the level of the water in *c*, serve for giving an outlet to the gas going along with the hot acid, and also for blowing through the pipes in cases of stoppage. This apparatus, which was first constructed by Mr. Stuart, of the Hebburn alkali-works,

is usually emptied and cleaned and examined every three weeks ; the cooling-water should be daily tested several times for acid with litmus-paper. The acid is thus easily cooled down from 130° C. at *e* to 36° C. at *f*, and can be used for absorption at the latter temperature without any fear, whilst even at 50° C. its absorbing-power is sensibly less, and of course still less at a higher temperature. In another, larger manufactory, there is a trough of 100 feet length by 4 feet wide ; the acid, first cooled from 132° down to 130° C. in a double spout, is further cooled in the trough down to 15° C., the apparatus cooling the acid for three sets of chambers of 140,000 cubic feet each.

A simpler but perfectly efficient cooling-apparatus exists in the works at Aussig, Stolberg, and others. The acid runs out of the Glover tower immediately into a cylindrical trough of thick lead, about 2 feet high and wide, and runs out of it again through a pipe coming away sideways from its bottom and turned upwards. In the trough there is a narrowly wound lead coil, through which cold water is continually running from above ; getting heated in the bottom part of the coil, it rises up and is taken away hot at the top. The cooling here generally goes down to 40° C., and is supplemented by letting the acid stand in tanks ; but 30° – 35° C. might easily be attained. This is a very rational method of cooling, because the hot acid running in at the top comes into contact with the upper, hot part of the water-coil, whilst the acid ultimately flowing away from the bottom, which is already cooled down to a great extent, is cooled still further by the cold water in the bottom of the coil. There is also no trouble caused by any deposit forming in the acid, if there is a sludge-valve provided in the bottom of the trough.

At some works I have seen a good cooler which I describe from notes supplied to me by Dr. Stahl. A flat pan, say 30 ft. long, 5 ft. wide, and 6 in. deep, made of wood and lined with 6 lb. lead, is divided lengthways into ten narrow channels by leaden strips, 4 inches wide and 6 inches apart. Each strip stops alternately 6 inches from the ends of the pan, so that a zigzag channel is formed, into which a 1-inch or $1\frac{1}{4}$ -inch lead pipe is laid, forming a coil of 200 feet in length. The acid runs through the zigzag trough, and cold water in opposite direction through the lead pipe. Where the hot acid enters, a double loose lining, made of 4 ft. length of heavy 2-inch pipe, cut open lengthways, is put into the trough



in order to protect it; this piece must be renewed about once every six months, and if this be observed the trough will not require any repairs for many years. A cooler of the above-stated dimensions suffices for cooling 18 tons of hot Glover-tower acid down to about 30° C. every 24 hours.

At large works the two systems of cooling just mentioned are sometimes combined. I consider as perhaps the best plan a perpendicular cooler, similar to that which has been adopted at several coal-tar works for cooling benzene vapours (*comp.* Lunge's Coal-Tar and Ammonia, fig. 115, p. 451); that is, two short, cylindrical or square boxes, one above the other, connected by a very large number (50 to 100) of narrow, perpendicular pipes, about 2 feet long and $\frac{1}{2}$ inch wide, the whole standing in a wider tank, supplied with cooling-water. Hot acid is run into the top box, slowly finds its way downward through the thin pipes, which possess a very large cooling-surface, and arrives cool in the bottom box, whence it rises up in a special pipe and is run off almost at a level of the top box. The bottom box must be provided with a sludge-valve. Or else the acid is contained in the outer tank, and cooling-water is run through the system of boxes and pipes just described.

Very efficient cooling might be produced by the action of a current of air, either by forcing this through the hot acid, or else by running this down a tower in which air rises up by the action of a fan-blast or by chimney draught; but where very large quantities have to be treated, the supply with cooling-air might require too much power to be economical.

In ordinary circumstances the absorption in the Gay-Lussac tower requires *at least* one half of all the acid produced. This is got from the Glover tower without any other cost but that of pumping up: in the case of other denitrating apparatus the cost of concentration has to be added to this. Frequently the necessary quantity of absorbing-acid is stated at a lower figure—for instance, as one third of the whole production; but this in most cases is certainly insufficient, and no doubt a large loss of nitre would be the consequence of it. On the other hand, manufacturers working with Glover towers, who, apart from the trifling expense of pumping, have no concentrating-expenses at all, send all their acid once a day through the Gay-Lussac tower. This is quite right. Bode ('On the Glover Tower,' p. 49) calculates that with a loss of 4 parts of nitre or 1.75 of N_2O_5 to 100 parts of acid of 170° Tw., the

absorption requires at least 56 per cent. of *all* the acid of 144° manufactured, if very strong nitrous vitriol (with 1.75 per cent. of N_2O_3) is to be obtained. Such strong nitrous vitriol, however, is not obtained in ordinary working; and therefore considerably more than 56 per cent. of all the acid manufactured must be run through the Gay-Lussac tower in order not to lose any nitre. In fact, some manufacturers send much more than their daily make through the Gay-Lussac towers; but at some of the best conducted works they manage with about $\frac{1}{4}$ or $\frac{1}{5}$ of the daily make. Of course, everything depends upon the style of working the chambers. With the ordinary style, where there is about 20 cubic feet of chamber-space to each lb. of sulphur burnt in 24 hours, the above-quoted figures are quite sufficient; but the forced style of work, sometimes adopted in France, where there is not much more than half the just-mentioned chamber-space, cannot be kept up except by a very large floating capital of nitre, and in this case twice or more the daily production of acid has to pass through the Gay-Lussac tower. I am, even in England, acquainted with two very large works (belonging to the same firm) in which the quantity of acid run down the Gay-Lussac towers is from three to four times the daily make; and in this case the ordinary chamber-space of 20 cubic feet is allowed. But it seems doubtful whether such an enormous feed of the towers is advantageous (apart from the cost of pumping), looking at the action of the coke on nitrous vitriol (pp. 160 and 519). At other works I have found $1\frac{1}{4}$ or $1\frac{1}{2}$ times the daily make of acid run through the Gay-Lussac tower, and so forth.

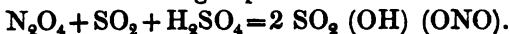
The specific gravity of the *nitrous vitriol*, as the acid issuing at the foot of the Gay-Lussac tower is called, does not differ very much from that of the acid fed in at the top. In the usual case, where there is ample chamber-space and the sulphuric acid is almost entirely condensed in the last chamber, the mixture still necessarily present in the exit-gases is, of course, absorbed by the stronger acid in the Gay-Lussac tower, and the nitrous vitriol running out at the foot is then 1° or even 2° Tw. weaker than the feeding-acid. But with the "forced style" of working at some French works there is a considerable quantity of acid contained in the exit-gases in the shape of mist, which is retained in the Gay-Lussac tower, and, added to the nitrososulphuric acid absorbed, may make the nitrous vitriol even a little stronger than the feeding-acid.

When properly treated, nitrous vitriol ought to be very little coloured, and ought to smell very little of nitrous acid; but on being diluted with water, especially hot water, it ought to effervesce strongly and to give off thick red vapours. At a few works this rough test is considered sufficient for judging of the quality of the nitrous vitriol; but at all the better works it is probably tested in the laboratory, which can be accomplished in a very short time by the permanganate method (*comp.* p. 177). Now and then this should be supplemented by a testing in the nitrometer, in order to make sure whether nitric acid is present or not. By these testings it can be seen from day to day whether the percentage of nitre increases or decreases. In the former case, if the other tests of the chamber-process agree with it, this is an intimation that some of the nitre must be taken off; in the latter case this test will, better than any other, show, before any damage has been done, that more nitre is wanted. In any case nitrous vitriol ought not to contain less than 1 per cent. of N_2O_3 ; above $2\frac{1}{2}$ per cent. it is too strong, and there is danger of nitrous gas escaping without being absorbed, which can be controlled by the colour of the "sight." In this case more strong acid must be charged at the top; and if there is an excess of nitre-gas in the chambers, a little less nitre must be used.

The Gay-Lussac acid, or nitrous vitriol, is essentially a solution of nitrososulphuric acid ('chamber-crystals') in sulphuric acid. Formerly it was believed that it regularly contained some nitrogen peroxide, or nitric acid (Winkler, Kolb, Hurter, Davis, &c.), but this assertion was only caused by the imperfection of the then employed analytical methods, as shown for Winkler's and Kolb's results by myself (*Chem. News*, vol. xxxvi. p. 147), the nitric acid being generated during the analyses themselves. The contrary fact, viz. that *ordinary* nitrous vitriol contains no appreciable quantity of nitric acid, was first proved by me; and it has been confirmed by several subsequent investigators. This is even the case when so much nitre has been introduced, intentionally, as in Lunge and Naef's experiments, or by inadvertence, that the last chamber contains some nitrogen peroxide (*Chem. Ind.* 1884, p. 10). It has been shown before (pp. 160 and 519) that this is no doubt due to a reduction of the nitric acid, originally formed from the nitrogen peroxide, by the coke packing of the Gay-Lussac towers. With columns filled with a non-reducing packing probably nitrous

vitriol containing nitric acid would be much more frequently met with; but with coke-towers and with the ordinary style of working, employed at all English and German and formerly also at all French works, it is one of the signs of the regularity of the process if *no* nitric acid occurs in the nitrous vitriol. Probably it is different with the French "forced style," where the chambers are made to turn out nearly twice as much as before, by supplying them with a comparatively enormous quantity of nitre (without, however, losing more of it in the long run, owing to correspondingly large Gay-Lussac towers). In this case it follows most distinctly, from Lunge and Naef's observations (p. 488), that there must be a *large* quantity of nitrogen peroxide in the last chamber, too large to be completely reduced by the coke to N_2O_3 , so that the nitrous vitriol will be found to contain some nitric acid.

A very strange error has for many years existed, both in all publications on the subject, and in the ideas of nearly all those practically concerned in the manufacture of sulphuric acid who gave any attention to the chemistry of the subject. This error is: that nitrogen peroxide, N_2O_4 , forms only a "loose" combination with sulphuric acid of such concentration as is employed for working the Gay-Lussac tower, and that, therefore, very little N_2O_4 is absorbed in that tower, unless it can be there reduced by SO_2 to N_2O_3 . This erroneous assumption, coupled with another error, viz. that the "nitre" in the chamber exit-gases consists essentially of N_2O_4 , and the *true* observation that the "nitrous vitriol" generated in the Gay-Lussac tower does not contain anything but N_2O_3 , has led to the invention of Brivet, Lasne, and Benker (G. P. 17,154), who introduce into the exit-gases, on their way between the last chamber and the Gay-Lussac tower, a certain quantity of burner-gas, by means of a steam-jet. The excess of moisture thus imparted to the burner-gas is taken out by means of a small coke-tower fed with Glover-tower acid, and the gas is now mixed with the chamber-gases before entering the Gay-Lussac tower. It was supposed that thus the nitrogen peroxide would be reduced:



No doubt this would be really the case if an appreciable quantity of N_2O_4 did exist in properly composed exit-gases; but we have seen that this is not so, at least with the ordinary, not "forced," work (p. 488). I have moreover conclusively proved (Berl. Ber. 1882, p. 488) that there is no foundation for the

assumptions underlying the above-mentioned patent, more especially the idea that N_2O_4 did not easily and completely dissolve in sulphuric acid of 142° Tw. In fact the first favourable reports upon the practical success of that patent process have not been confirmed by subsequent observations, and it must be held that for properly-managed chambers that process offers no advantage.

The success of the working of the Gay-Lussac towers depends also upon the proper *regulation of the draught*. If the draught is insufficient, the chamber-process will from the outset be injured by the continual leakage of gas and by all the other drawbacks enumerated before, and especially by the behaviour of the pyrites in burning. In that case the Gay-Lussac tower itself will not work properly; for unless oxygen be present in the last chamber before the gas leaves it, there will be unoxidized nitric oxide left, which will pass through the tower unabsorbed and only form red vapours when issuing into the outer air. At the same time there will be sulphurous acid present in this case; and this acts still worse, since it decomposes the nitrososulphuric acid still present in the vitriol with which the coke in the tower is soaked, and carries away its nitre as nitric oxide. If the waste gas, as previously insisted upon, contains 5 or 6 per cent. of free oxygen, the above cannot happen to an appreciable extent, except, as some assert, in the presence of much arsenious acid.

If, on the other hand, the draught is too strong, therefore with poor kiln-gas, the sulphurous acid will not have time to condense within the chambers as sulphuric acid; it will partly get into the tower, and there cause the decomposition just mentioned and loss of nitrous compounds.

In both cases, therefore, the same consequence will happen as if the last chamber did not contain an excess of nitre-gas; and if nitre is too much economized, it will indeed be wasted all the more in the way just described, the sulphurous acid driving off the nitrogen of the tower-acid into the air in the shape of nitric oxide.

Such a faulty working of the tower will announce itself by the escape of red vapours out of the chimney, by the tests of the tower-acid, and even by its appearance, since the vitriol, which otherwise is nearly or quite colourless, turns of a dark purple, and is filled with countless small bubbles of nitric oxide, at the same time getting heated by the formation of sulphuric acid (Bode, in a note to the translation of H. A. Smith's pamphlet, p. 122). It is

therefore the worst case of all, if alternately sulphurous acid gets into the tower and the reverse. In that case nitrous vitriol is alternately produced and decomposed again. When, however, sulphurous acid constantly passes into the tower, there is no absorption of nitre-gas at all, and the tower in this case does not act as an absorbing apparatus, but simply as a continuation of the chamber-space (Bode, *ib.* p. 124). This proves, as Bode justly remarks, that one improvement, viz. the recovery of the nitrous acid, necessarily led to another, viz. to a better condensation of the sulphurous acid, or a better yield on the sulphur burnt.

Various plans for recovering the Nitre in other ways.

Merely for the sake of completeness be it mentioned that several other plans have been proposed for utilizing the nitre-gas escaping from the chambers. Not one of them has ever possessed any practical value; and they can hardly be said to possess even an historical value, since they have never been employed except in a few isolated cases. Kuhlmann, for instance, employed 30 Woulfe's bottles, the first ten of which were filled with water, the second ten with a solution of barium nitrate, and the third ten with barium carbonate suspended in water; the mixture resulting in the last ten bottles was used in the second ten bottles, where barium sulphate ("permanent white" or "blanc fixe") was precipitated. Others have used milk of lime, ammoniacal liquor, or even pure water for the absorption of the acid vapours. All these plans are so very much less advantageous or complete than Gay-Lussac's process that they cannot at all compete with it.

G. Wachtel (*Dingl. Journ.* vol. 245, p. 517) proposed forcing the exit-gases by means of a Körting's injector through a red-hot iron or fire-clay retort filled with iron turnings. Here the nitre-gas is to be reduced to ammonia which is to be absorbed by hydrochloric or sulphuric acid. Nobody seems to have been rash enough to make a practical trial of this plan.

Denitration of the Nitrous Vitriol.

The operation going on in the Gay-Lussac towers whose final result is the production of an acid more or less charged with nitrous compounds, viz. the "nitrous vitriol," requires for its

necessary complement another operation, by which the nitrous vitriol, which by itself has no practical use, can be reintroduced into the chamber-process, both in order that the absorbed nitrous compounds may be restored, and that the sulphuric acid originally employed may be recovered in a pure state. It cannot be denied that Gay-Lussac was not sufficiently successful in completing his invention (which has been so important and useful for the manufacture of sulphuric acid) in this particular; and it is more than probable that the slow extension of his process, nay, even the far from exceptional abandonment of it where it had been introduced in the first instance, must be attributed to the fact that the denitration of the nitrous acid was attended with too many difficulties, expenses, and breakdowns of apparatus. The invention of the *Glover tower*, which does away with all this, must therefore be considered almost equally important with that of the Gay-Lussac tower itself; and in fact the *general* introduction of the latter only dates from the time when manufacturers were able to combine it with the Glover tower.

The various contrivances for denitrating nitrous vitriol have been described and criticised thoroughly and in detail by Fr. Bode, in 1876, in a paper "On the Glover Tower," which obtained the great prize of the Berlin Society for the Promotion of Industry; and this essay has been used to a great extent in the following description. Bode's paper has also been published by instalments in 'Dingler's Journal,' vols. ccxxiii. to ccxxv.

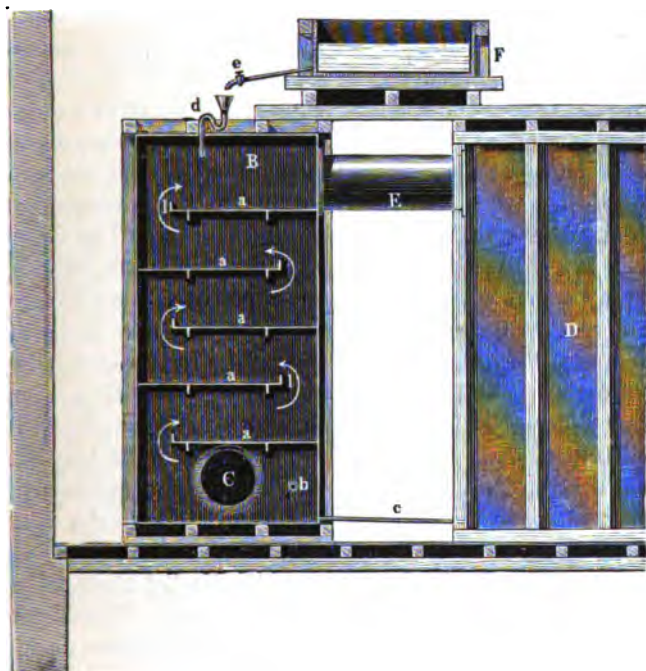
The methods for denitrating nitrous vitriol are founded, on the one hand, on diluting it either with hot water or steam, or with a combination of both, or, on the other hand, on the action of sulphurous acid, mostly along with a certain amount of dilution. That in these cases the nitrososulphuric acid is completely decomposed, either by the dilution or the action of the sulphuric acid, has been proved in detail from theoretical investigations. We shall now treat of the apparatus and modes of procedure employed in practice for that purpose.

One of the oldest apparatus was described in Payen's 'Chimie Industrielle,' and has been copied out of this into most text-books; it may be called the "shelf apparatus." It is described in Schwarzenberg's work as follows:—

"This operation can be carried out in a small lead chamber, shown in fig. 219 in section at B. The nitrous vitriol is first con-

veyed into the tank F, placed above the chambers, and from this flows into the chamber through the cock *e* (by which its flow is regulated) and the bent funnel tube *d*. The chamber is provided with horizontal shelves, *a*, over which the acid runs down. They are burnt to the chamber-walls on three sides; and on the fourth side there is a small upstanding margin, *l*, for retaining a layer of liquid about 4 inches in depth. The gas enters the chamber direct from the sulphur-burner through the tube C, a little above the bottom of the chamber; the pipe *b* introduces the necessary steam in the same place. The latter decomposes the

Fig. 219.



liquid standing on the shelves *a*, whilst passing over its surface, carrying along the gases. On the top the gaseous mixture, along with the nitrous acid set free, passes through the pipe E into the large lead chamber, whilst the sulphuric acid deprived of nitrous acids runs through *c* into the bottom of the same chamber."

Another apparatus, constructed on the same principle as that just described, is the "Dénitrificateur" proposed by Gay-Lussac himself. It is a lead column of square or circular section, provided with a grating a little above the bottom, and packed with coke on the top of this. The nitrous acid runs in at the top, and is scattered by means of a rose. Below the grating the gas of the sulphur- or pyrites-burners enters and meets the nitrous vitriol descending; at the same time either a jet of steam is introduced separately, or the gas is previously conducted through tanks filled with water, in order to be saturated with moisture.

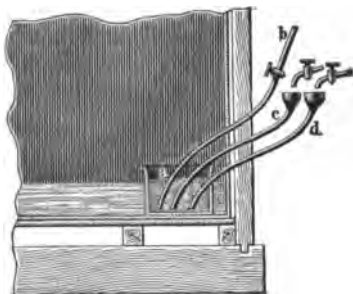
In these apparatus the denitration evidently took place by the joint action of the steam and the sulphurous acid. The acid ought to arrive at the bottom entirely free from nitrogen compounds; but it is then so dilute that it must be run back into the chambers. Such apparatus are hardly to be found in use in any place now-a-days, for good reasons. Since the acid is in them diluted to the same extent as in the process of denitrating by hot water or steam alone, they present no advantage over the latter; indeed they were in the first instance replaced by the latter processes. But the apparatus just described have this drawback, that they last a very short time, on account of the rapid destruction of the lead. The destructive action is always very strong in the first chambers, which, even under the best conditions, and in the presence of a Glover tower, suffer more than the remaining chambers, and have to be made of thicker lead if they are to last as long. The reason of this is partly the heat of the gas, partly the nitrous compounds themselves. It is evident how much more of this action must take place in a very small chamber, such as the "shelf apparatus" or Gay-Lussac's "Dénitrificateur." The worst, however, of these apparatus is that the steam introduced into them necessarily leads to the condensation of very dilute sulphuric acid and nitric acid on the sides of the apparatus, which must rapidly corrode the lead. Bode calls attention to another very important circumstance. Considering the small size of the chambers serving as shelf apparatus or dénitrificateurs, any changes in the chamber-process, in the composition of the kiln-gas, of the supply of steam, of the outer temperature, &c. must be felt in them very much more than in a large lead chamber. Therefore, from time to time, stronger nitrous vitriol will condense on the walls, and be diluted directly after by an increased condensation of water, and thus become charged with nitric acid. As every practical man knows, the interior walls of a working

lead chamber are always covered with a white slimy lining of lead sulphate, which holds back acid like a sponge, but at the same time protects the lead from further action, until such time as the acid is diluted by condensed steam, gas is given off from it, and the slimy mass of lead sulphate is loosened and washed off, whereupon the lead is again exposed to fresh attacks. The older denitrating-apparatus, therefore, were exposed to very rapid destruction, because they employed the simultaneous action of sulphurous acid and of steam, and were therefore soon abandoned.

In England, most manufacturers passed over to *diluting the nitrous vitriol* in separate small boxes *with water and steam*, whilst on the Continent usually "steam columns" or "cascades" were preferred. The English arrangement, such as was almost general in former years, and has only been thrown into the background by the Glover tower, is shown in fig. 220. *a* is a lead vessel, about 1 foot high and 18 inches wide, which stands within the lead chamber, very near the inlet for the kiln-gases.

Three pipes, *b*, *c*, and *d*, lead into *a*, passing through the side of the chamber and burnt into it. Of these *b* conveys steam, *c* water, and *d* nitrous vitriol; *c* and *d* end in funnels, through which the liquids run. The steam comes from a steam-boiler. The vessel *a* is first filled with water; this is

Fig. 220.



then heated to the boiling-point by steam; and now steam, water, and nitrous vitriol are admitted in such proportions that the latter is completely denitrated before it can run over out of the box *a*. The proximity of the gas coming from the pyrites-burners acts in this way: the escaping oxides of nitrogen are at once spread through the chamber and are mixed with the other gases; and at the same time the gas protects the lead against corrosion.

More perfect is the arrangement formerly usual on the Continent, where the denitration takes place on *cascades*, entirely similar to those described previously (p. 408), only with the addition of a contrivance for introducing hot water.

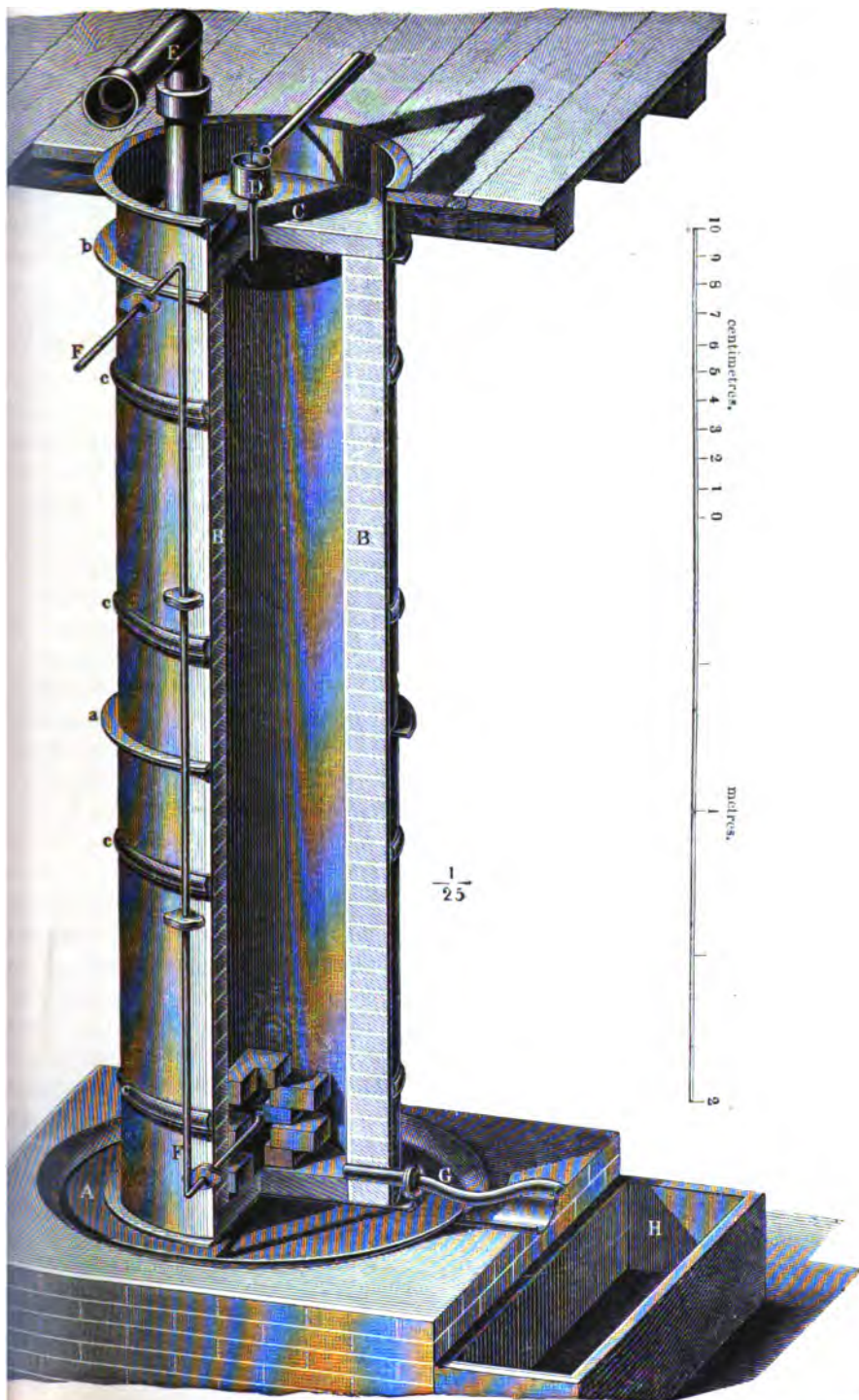
The *denitration by steam alone*, or by steam with very little water,

takes place in the so-called *steam-columns*, of which we here describe one of the most usual forms as follows:—

Fig. 221 represents a steam-column on a scale of 1 : 25. In the diagram a piece of the side is cut out to show the interior of the apparatus. It consists of a cylinder about 11 feet 6 inches high and 3 feet wide, standing on a solid piece of masonry. It is made of strong sheet-lead, and composed of three pieces, whose joints, at *a*, *b*, are burnt together. The bottom, *A*, is united to the cylinder in the same way. Four strong iron hoops, *c*, increase its stability. In order to protect the lead against the corrosive action of the hot acids, it is provided with a lining, *B*, of hard-burnt fire-bricks, which are specially moulded for this, and ground together so as to make a tight joint. The joints are grouted with a mortar made of ground fire-clay. On the top the steam-column is closed tight by means of a slab of fire-clay resting on the brick lining. In the centre of the cover the lead pipe, *D*, serves for feeding the column with nitro-vitriol. Its funnel is closed with an acid lute. Beside this the stoneware pipe, *E*, is put tight into the cover, for taking the nitrous acid away into the chamber. Sometimes these pipes are surrounded by a jacket of lead, in order to avoid any interruption of work by their cracking. The steam is introduced into the column through the pipe *F*, near its bottom, at such a height that the mouth of the steam-pipe remains above the sulphuric acid collecting there. This mouth is covered up and built round with bricks in such a way that proper channels remain for the steam and the acid. On the top of this the column is filled with bits of flint nearly up to its cover; they are about the size of a fist near the bottom, and decrease towards the top to the size of a walnut. In the place of these some works use bits of broken stoneware. The nitrous vitriol running in at the top trickles down through the bits of flint, and is decomposed in this way by the rising steam. Whilst the nitrous acid given off from it goes away into the chamber through the pipe *E* in the state of vapour, the sulphuric acid, diluted by the condensed water, arrives at the bottom of the steam-column, and runs through the pipe *G* into the tank *H*. The pipe *C* is so bent as to remain always luted by the acid.

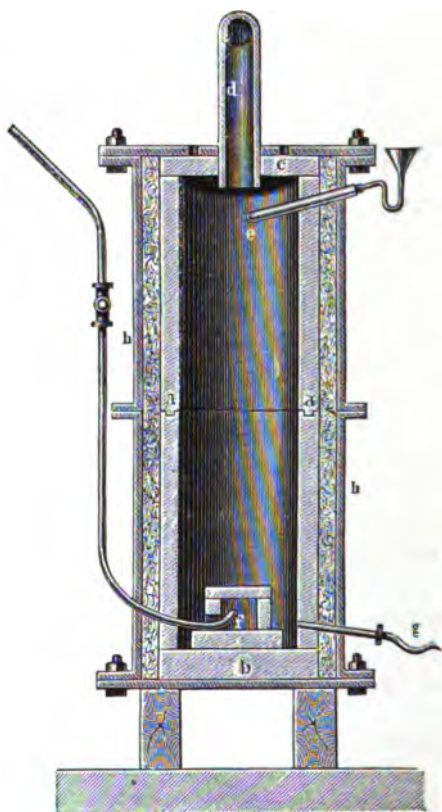
According to Bode, such a column, at the Royal Saxon factories at Freiberg, sufficed for a system producing 125 cwt. of sulphuric acid of 170° Tw. in 24 hours. He further remarks that the bottom of the cylinder is not joined to the lead saucer *A*, but

Fig. 221.



stands loose in it. He also remarks, very justly, that the fire-bricks forming the lining must be boiled in coal-tar, and joined with tar mortar, not with ground fire-clay alone. Such ground fire-clay would not only, as Bode says, be washed out, but it might swell, by the formation of aluminium sulphate, and lift off the cylinder-cover. The tar mortar is made by kneading together finely ground fire-clay with coal-tar, thickened by boiling. It must form a perfectly homogeneous, plastic mass—which is effected on a small scale by beating with a mallet, on a larger scale by grinding under edged runners.

Fig. 222.



In a large factory near Newcastle there existed, till 1873, steam-columns consisting of a cast-metal pipe 3 feet wide and 9 feet high,

with a lining of lead and another lining, inside the first, of thin bricks (2 inches), and a packing of flints. Since then they have been replaced by a Glover-tower.

There are also steam-columns made without a lead jacket; but they cannot then be built up of bricks, but must be made in one or two pieces. Bode figures such a column, erected by Dr. Gilbert at Hamburg (fig. 222). Its inner diameter is 1 foot $3\frac{1}{2}$ inches, its height 13 feet 1 inch. It consists of two gas-retorts, *a a*, made tight at the joint, after heating the same, by asphalt. The bottom, *b*, and the cover, *c*, are formed of round fireclay-slabs; the latter contains an opening for the stoneware pipe *d* for carrying off the nitre-gas and the excess of steam into the chamber. The nitrous vitriol enters at *e*, the steam at *f*, and the denitrated sulphuric acid runs off at *g*. The retorts are surrounded by the cylinders *h h*, of $\frac{1}{2}$ -inch cast iron, which are bolted together and to the cast-iron top- and bottom-plates. A space of $1\frac{1}{2}$ inch remains between the cast iron and fire-clay, and is filled with melted asphalt having a very high fusing-point. The column is filled with bits of flint; the mouth of the steam-pipe is protected by loose bricks. This apparatus in Bode's time had been in operation for five years without giving any trouble, and supplied a set of chambers making 6 tons of acid of 170° Tw. in 24 hours.

In other works the steam-columns are made much smaller, which is evidently quite sufficient. In Würtz's 'Dictionary of Chemistry,' iii. p. 157, Scheurer-Kestner figures a column made of a piece of lava 6 feet 6 inches high, and only 8 inches wide inside, 2 feet outside, filled with broken glass. Otherwise it offers no peculiarities.

As late as 1890 I found in Hamburg a steam-column of the following construction. It consisted of a cast-iron cylinder, lined with bricks inside; the bottom part, about 8 inches, consisted of lead and dipped into a very thick cast-lead dish, forming a hydraulic lute, just at the point where the steam entered. The outflowing acid was kept at 112° Tw.; it tested on an average 0.05 per cent. N_2O_5 and 0.01 per cent. NO_3H , which seems very good work for that strength.

The simplest and cheapest apparatus for this object, as Bode asserts, are stoneware Woulfe's bottles of about 55 gallons capacity, as shown in figs. 223–225. They are filled with bits of flint. Of the two bottom branches, *a* and *b*, one serves for running off the dilute acid, the other for the steam-pipe. The nitrous gas escapes

Fig. 223.

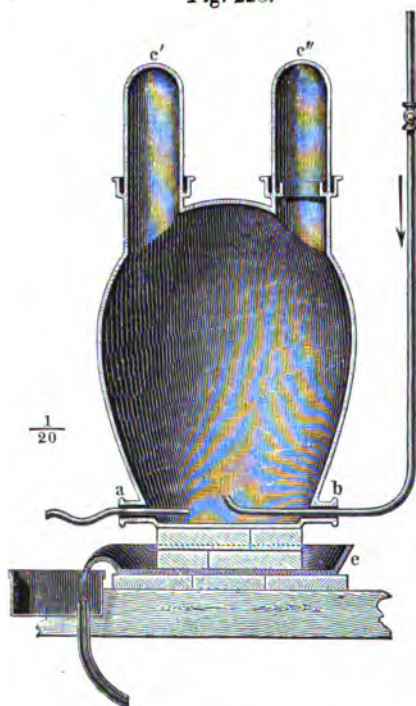
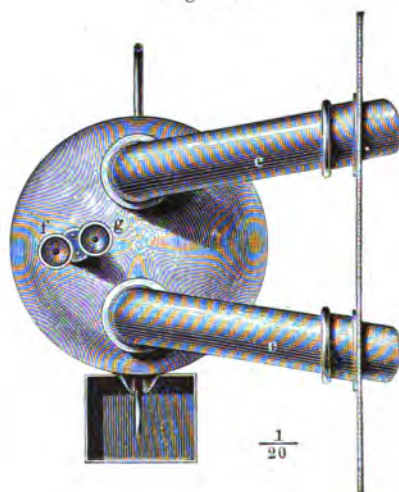


Fig. 224.



Fig. 225.



through the two pipes *c c*, joined to the jar with cement (like *c'*), or by a hydraulic lute (like *c''*). The pipes *c* are continued into lead pipes having some fall towards the chambers. The jar stands in a stoneware saucer, *e*, on a foundation of fire-bricks; through *f* nitrous vitriol, through *g*, in case of need, water is introduced. If one jar is not found sufficient, a second one can be put up at very little expense. (It is very much to be feared that such jars will not last a very long time.)

The first exact comparison between steam-columns and cascades, touching their capacity and expense of working, was made by Bode in his prize essay. His conclusions were as follows:—As to first cost of erection, a complete steam-column is dearest, next to it a cascade; the cheapest are the jars, even if several of them have to be employed. In the steam-columns and the jars the acid can be completely denitrated, so that it will give no reaction with sulphate of iron; with cascades it is not possible to go so far; but, for all that, no more nitre seems to be used with the latter. In the steam-columns the most vulnerable part is the stoneware pipe for taking away the gas; in the cascades, the junction-pipe between the two lead pots. Bode also quotes, as a drawback of the steam-columns, that it is mostly necessary to *pump* the acid out of them into the chambers, because they are mostly placed on the ground; but this I think wrong. In the factories visited by me, I have always found the columns placed high enough for the acid to run direct out of them into the chambers. If the nitrous acid has to be pumped to the top of the steam-column, this will not be appreciably higher than to the top of the cascades. Bode on the whole prefers the jars, if no Glover tower can be erected; but he makes a condition very difficult of fulfilment, viz. that the jars be of a material capable of resisting the heat. So far as my experience goes, I have never seen jars of 55 gallons which could hold out for any length of time against the successive action of cold nitrous acid and of steam; and I should advise any manufacturer not to practise such economy in a matter of very small moment, but to prefer to perishable stoneware jars a single piece of lava or of basalt, although these materials also cannot be said to be everlasting. The small size mentioned by Scheurer-Kestner is quite sufficient.

The expense of denitrating in steam-columns and cascades has been calculated by Bode (Prize Essay, p. 48), so far as this is possible, considering the many circumstances coming into play. But since

for these calculations such a number of arbitrary assumptions have to be made that the results cannot be applied to real cases, we will only remark that, according to them, the denitration in steam-columns is dearer than that on cascades, as may be imagined beforehand—the former consuming a great deal of steam, the latter little or none, if hot condensation-water be used. Many manufacturers preferred the steam-columns to the cascades, as in the former the denitration is much more under control than in the latter, or in the boxes described, p. 563. On the other hand, at the Oker works (*cf.* Bräuning, *l. c.* p. 141) the steam-columns previously erected were abandoned owing to their continuously breaking down; and they were replaced in the older sets by cascades, in eight more recent sets by Glover towers. It was found there that the cascades often yield sulphuric acid containing nitric acid; and therefore a steam-injector was fixed to the first small chamber, by which the strength of the acid in this chamber was reduced to 110° Tw.

At Freiberg, in 1890, steam-columns were still used for denitrating nitrous vitriol, and the fresh nitric acid was introduced by means of cascades. The reason for retaining these apparatus was this, that the gases at those works enter the chambers at the temperature of the surrounding air (*comp.* p. 473), and it was assumed that this is too low for working a Glover tower; but it is doubtful whether this assumption is correct (see later on).

Glover Towers.

The apparatus which is now used for denitration in all but exceptional cases is the *Glover tower*, which is properly treated in this Chapter, since its inventor had in the first instance constructed it for denitration, although it might just as well be described as a cooling and as a concentrating apparatus. The Glover tower was invented by Mr. John Glover, of Wallsend, near Newcastle-on-Tyne. According to personal information received from Mr. Glover, he had built his first tower already in 1859, at the Washington Chemical Works, near Durham. This tower was made of fire-bricks, and packed with a network of thin fire-tiles. It lasted a year and a half, and proved the correctness of the principle. In 1861 Glover, at the same place, built a lead tower; and when founding another works at Wallsend in the same year, he, of course, built a similar tower there as well, which worked until 1863 or

1864. From the experience gained in this way, Glover constructed in 1864 a third tower, which, in all essential points, was the same as is used to this day. Up to that time only his nearest neighbours had introduced the tower. It must here be observed that its inventor had not only taken out no patent for it, but, with great liberality, showed it to every one interested in the matter. In spite of that, some of the manufacturers on the Tyne, intending to "improve" the tower, committed mistakes in its construction; and, at least in one case, this led to its being given up again, although it has since been reintroduced. Between 1868 and 1870 all the larger and better-managed works on the Tyne introduced the Glover tower; it was adopted in Lancashire about 1868, at London in 1870. Until 1871 nothing had been published about the Glover tower; and it was entirely unknown outside a number of English alkali-works till I published a paper on it in 'Dingler's Journal,' vol. cci. p. 341, which made it generally known in Germany, and led to its adoption in that country. The objections raised against the tower as a denitrating apparatus (nobody has ever doubted its excellence as a concentrating and cooling apparatus) have been completely refuted. The first objections raised by Bode ('Dingler's Journal,' ccii. p. 448) were immediately refuted by me (ib. p. 532), and have since been withdrawn by Bode himself. Bode has become one of the most zealous constructors and advocates of the Glover tower. Also the objections raised by M'Culloch (Chem. News, xxvii. p. 135) have been answered by Glover (ib. p. 152), by me (ib. p. 162), and Bode (Prize Essay, p. 5). M'Culloch himself afterwards changed his opinion. Much more serious objections have been made by Kuhlmann (Hofmann's Official Report, i. p. 174) and by Vorster ('Dingler's Journal,' ccxiii. p. 506), on the assumption that the contact of hot sulphurous acid and nitrous vitriol in the tower causes a considerable loss of nitre compounds in the shape of nitrous oxide or of free nitrogen. It is certainly a fact that, under certain conditions, hot sulphurous acid reduces the nitrogen oxides down to nitrous oxide or even to nitrogen. But that such conditions exist in the Glover tower Kuhlmann could not prove, because he had none at his disposal; nor has Vorster experimented with the tower itself in this direction, although he made other interesting observations respecting it; but, entirely on the strength of laboratory experiments, he asserted that 40 to 70 per cent. of the nitrous

compounds were lost in the Glover tower. His experiments, however, were made under totally different conditions from those existing in the Glover tower; and I succeeded in reducing Vorster's inferences on the loss of nitre *ad absurdum* from his own figures ('Dingler's Journal,' ccxv. p. 56, ccxvi. p. 79). In the experiment considered by Vorster the most conclusive, he passed hot sulphurous acid mixed with air for 27 minutes through nitrous vitriol heated to $180^{\circ}\text{C}.$; and it is inconceivable how he could assert that this condition answers to that in the Glover tower. Into this the nitrous vitriol enters quite cold, mixed with chamber-acid; and only on leaving, when its heat is greatest, does it attain $130^{\circ}\text{C}.$ It is out of the question that it should have that temperature in any considerable part of the tower, much less 180° , as in Vorster's experiment. On the contrary, that acid which shows a little higher temperature (but never as high as in Vorster's experiments) contains next to no nitrous acid, but is only further concentrated by hot kiln-gas; and, at all events, the denitration takes place to the greatest extent in the upper part of the tower, where the acid is still pretty cold. This follows with certainty from the well-known fact that the denitration of dilute acid takes place readily, that of concentrated acid with great difficulty. Apart from this, the acid is never exposed to the current of hot sulphurous acid so long as in Vorster's experiments. If once the packing has been quite impregnated, the acid gets from the top to the bottom in a few minutes; but, owing to its fine division, it is almost entirely denitrated near the top. In short, Vorster's experiments must be called worthless for deciding the matter in question, even if they were not refuted by the plain fact, that with the Glover tower the waste of nitre is *at least* no higher than with any other process. More about this below.

Subsequently (Berichte der deutschen chem. Gesellsch. i. p. 1432—more explicitly in 'Dingler's Journal,' 1877, ccxv. p. 474) I criticised in detail the experiments and statements of Kuhlmann and Vorster, and proved their irrelevancy. I further proved by experiments that, if the sulphurous acid gas is mixed with a similar excess of oxygen as in the kiln-gas, this mixture decomposes nitrous vitriol, even at a temperature of 200° (in the Glover tower it never gets beyond 130°), in such a way that the *whole* of the nitrogen oxides can be recovered by absorption in concentrated sulphuric acid. Pure sulphur dioxide, free from

oxygen, does not act on nitrous vitriol at 110° – 130° , but only at 200° C., in such a way as to cause the formation of some nitrous oxide. This, however, is not a practical case at all; and it remains a fact that in the Glover tower neither nitrous oxide nor nitrogen are formed in appreciable quantities. My experiments and calculation were attacked as inexact by Hurter ('Dingler's Journal,' ccxxvii. pp. 465 & 563), but were completely vindicated by me (ib. ccxxviii. pp. 70 & 152).

If there were any truth whatever in Kuhlmann's and Vorster's assertions, it would certainly be a cause of still greater loss when the fresh supply of nitre-gas is carried through the tower, as is done in the great majority of English, or when even the liquid nitric acid is run through it, as in most continental works. Then not merely 70 per cent. of the nitrous vitriol, but also 70 per cent. of the fresh supply of nitre, or nitric acid, would be wasted by the tower. This certainly would be felt in a very sensible manner. But already in 1871, of the ten works on the river Tyne which possessed Glover towers, only three worked so as to decompose the nitre by the gas of separate pyrites-burners, and to take the gaseous mixture past the Glover tower direct into the chambers. The other seven works sent the gas of *all* burners, along with all the fresh nitre-gas, through the towers, *without consuming any more nitre* than the three former ones. Among these three works was that managed by myself, and in my first publication I recommended this arrangement. Later on, from experience gathered in the meantime, the plant was altered, and *all* the kiln-gas, along with the nitre-gas, was taken into the Glover tower; but no extra consumption of nitre whatever could be detected. In the same way Mr. Schaffner, of Aussig, found no extra consumption ensue when he began introducing all the liquid nitric acid through the Glover tower.

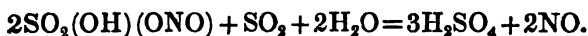
Glover himself reports (Chem. News, xxvii. p. 152) that he had consumed, for 1651 tons of sulphur (from Norwegian pyrites), only 63 tons 13 cwt. of nitre, = 3·8 per cent., with a chamber-space of 20 cubic feet to 1 lb. of sulphur burnt in 24 hours. His pyrites only contained 40 per cent. of sulphur, as I know very well, since I used the same quality at that time; the conditions of work were therefore not so favourable as with richer ores. At the same time Glover concentrated all his chamber-acid to 140° – 150° ; and this is a common experience in most works.

The most important argument is this: it is absolutely certain from the practical experience of many works, that with the Glover tower rather less nitre (never more) is used than with steam-columns or cascades. This is witnessed, for instance, by the former opponent of the Glover tower, Bode, in 'Dingler's Journal,' cccvii. p. 305, and in his prize essay, p. 87; and, altogether, no contrary statements of those who have had practical experience of the tower have been given to the world. On the contrary, the Glover tower has not only been generally accepted in England, but also on the Continent. Already in 1875 the Berlin Society for the Promotion of Industry offered a prize for an essay on this subject, in which the utility of the Glover tower for most cases is expressly presupposed, and only its applicability for kiln-gas of inferior heat is mentioned as doubtful and requiring examination. The result of this was Bode's often-mentioned essay on the Glover tower. Now-a-days the Glover tower forms an essential part of every well-arranged sulphuric-acid works, and holds the same rank with the Gay-Lussac tower. Certainly it will not answer to the expectations when constructed in an improper way or from unsuitable material, and therefore, at first, was here and there abolished again; but the same thing must be said of every apparatus used, in the whole range of industry; and the *consensus* of the great majority of manufacturers has entirely decided for the Glover tower. Bräuning (*l. c.* p. 140) also quotes the experience of a whole series of works at Oker in which the tower is employed, and where, since its introduction, less nitre is used than before, in consequence of the acid being completely denitrated, so that no loss can be incurred through the reduction of nitric acid to nitrogen or nitrous oxide. On my extensive tours through a number of the best English, German, and French alkali-works, I have everywhere received the same information, viz. that since the introduction of the Glover tower less acid is consumed than formerly (with the diluting process). This may very frequently be in consequence of the chamber-acid being also denitrated in the Glover tower; but in some works the acid of the large (or first) chamber is not kept nitrous at all, and in others, from various causes, only a small portion of the chamber-acid passes through the Glover tower. In no case is there the slightest reason for asserting that the Glover tower, by itself, wastes more nitre than the diluting process. At Malétra's works at Rouen, before the introduction of

the Glover tower, 2 parts, after it only 1·3 part of nitre has been used to 100 parts of pyrites.

It must not remain unmentioned that Cl. A. Winkler, in 1867 (*l. c.* p. 24), proposed very clearly the denitration of nitrous vitriol by sulphurous acid, without having any knowledge whatever of the fact that this plan had been carried out for some years in practice by Glover and others. Moreover Winkler's plan was vitiated by his proposal to add a small quantity of water. He evidently had no idea of the concentrating action of the apparatus which is now called the Glover tower.

Functions of the Glover Tower.—Although outwardly resembling a Gay-Lussac tower, its function is exactly the opposite of that of the Gay-Lussac tower—viz. to deprive the nitrous vitriol running off *at the bottom* of the Gay-Lussac tower of its nitrous compounds, and to restore it to a proper state of concentration for applying it again *at the top* of that tower. This, certainly, is only one of the functions of the Glover tower, but the most important and characteristic of all. The tower fulfils this function by exposing the nitrous vitriol, usually mixed with chamber-acid, in a finely divided form, to the action of the hot burner-gas, whose heat acts concentrately upon the sulphuric acid, and whose sulphurous acid acts denitratingly upon the nitroso-sulphuric acid; and the simultaneous concentration and action of the sulphurous acid seem very much to advance the denitration, which takes place according to the equation :



Glover's apparatus cannot be put in the same line with the apparatus described above (p. 560 *et seq.*), because in it no condensation of dilute vitriol containing nitric acid can take place on the lead walls, and because it is altogether so constructed that the lead nowhere comes into contact with the hot gas and the nitrous vitriol. Once properly built, it goes on working for many years, and causes no interruption of the process. Besides, it possesses two very great advantages. The first is, that it is both the most complete and the most rational of all cooling-contrivances for the burner-gas :—the most complete, because the gas is brought into immediate contact with the cooling-liquid in the shape of a fine spray, not separated from it by a metallic wall or only exposed to the cooling-action at the circumference of the current; the most

Fig. 226.



Fig. 227.



rational, because no expense has to be incurred for pumping up cold water for cooling, but the generated steam is at once usefully employed in the chamber. The second and still greater advantage of the Glover tower is that in it not only all the acid serving for absorption in the Gay-Lussac tower, but the whole of the chamber-acid is brought to 144° or even up to 152° Tw. without any expense except that of pumping the acid to the top of the tower—an expense which is very small indeed, especially in the case mentioned on p. 536, where the exhaust-steam of the air-pumping engine is used as steam for the chambers.

The Glover tower is, moreover, now mostly used for introducing the requisite fresh nitric acid into the chambers without any special apparatus, by running it down along with the nitrous vitriol. Before it arrives at the bottom it is fully denitrated, as well as the nitrous vitriol itself.

Even a solution of nitrate of soda has been employed in a similar way, but this has been given up as impracticable (p. 413).

Before entering on a detailed explanation of all these functions we will describe the construction of a Glover tower.

The following is a description of a Glover tower erected by me in 1873, which served for a chamber-space of about 160,000 cubic feet and a daily consumption of 9 tons of 48-per-cent. pyrites. The following diagrams and descriptions are, of course, only meant to serve as an instance of a tower that worked well, but do not claim to be authoritative in all details. Fig. 226 is a front elevation; fig. 227, a sectional elevation through the line AB (fig. 228); fig. 228, a sectional plan through CD (fig. 227); fig. 229, a section through the lead, in order to show the way in which the sheets are joined together; fig. 230, a view from the top, showing the acid-distributor and the man-hole. Figs. 231 & 232 are sectional plans, showing a different arrangement for a grating, viz. fig. 231 below, and fig. 232 above the same.

The *foundation* consists of two pillars of ordinary good brickwork, joined by a fourfold arch and braced together by railway-rails and tie-rods *a a*. (In lieu of this ordinary railway-rails may be placed across the pillars, which makes the foundation much lighter and allows free access to the bottom of the tower; and the pillars themselves may be made of cast-iron. In fact modern Glover towers are usually erected on such iron foundations.) The top of the foundation forms a platform which is covered with a

lead apron, *b*, of 7 lb. to the square foot, the sole object of which is to secure that in case of leakage of the tower-bottom the acid cannot get to the brickwork, but must run off sideways. Instead of turning this apron down, it can be turned up in the

Fig. 228.

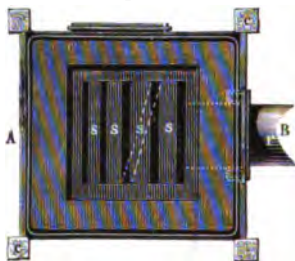


Fig. 229.

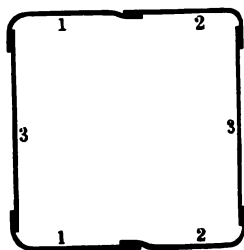


Fig. 230.

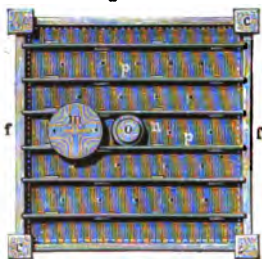


Fig. 231.

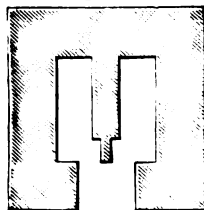
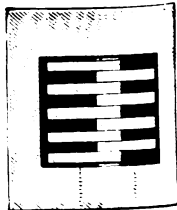


Fig. 232.



shape of a saucer with a spout; and if this be kept full of water it will contribute to the conservation of the inner saucer, by keeping this at a moderate temperature.

Sometimes the platform at the top of the foundation is covered with a molten mixture of pitch and brimstone, and the leaden apron is put upon this while still warm. This is an absolute protection against any corrosion of the iron pillars and girders by any acid finding its way down.

The tower itself is erected within a strong frame of pitch-pine which at the same time carries the necessary tanks. Four pillars *cc*, 12 inches square, which are with advantage placed on stone ware slabs to protect their feet from being corroded by acid running over, are joined together by joists 6 inches square mortised in such a way that they can be knocked out upwards when they have got damaged, whilst the weight of the lead other

wise pulls them downwards. To effect this, the mortise-holes in the uprights are continued upwards in a slanting direction; figs. 226 & 227 show this clearly at *ee*. At the top of the tower stronger joists, *ff*, 6×9 in., run all round; these have to support a greater weight. Instead of this kind of frame, the ordinary frame with diagonal stays can be employed; in this case the whole weight of the lead must be carried by the top joists, because the lower joists are missing. At the top the uprights are tied together by the crown-trees *gg* (12×12 in.); on these a wooden cabin is erected, within which the acid-tanks are placed. There is, properly speaking, only one tank, which is divided into two by a partition; it stands on the joists *hh*; and its wood construction can easily be seen from the figure. Both compartments are lined inside with lead of 7 lb. to the square foot; one of them receives nitrous vitriol, the other chamber-acid by the distributing-box *i* (details in figs. 236 & 237, p. 588), to which the acid is conveyed from the delivery-pipe of the higher Gay-Lussac tower, either by means of a special splashing-apparatus (as in fig. 210, p. 542), or, omitting the box *i*, from a distributing-box with 3 plug-valves, common to them and to the Gay-Lussac tower (as in fig. 211, p. 543). The latter is the proper thing when both towers are placed side by side, and when their tanks are covered by the same wooden house, which is by far the best arrangement; in that case the tops of the two towers are placed at the same level; but the foundations of the Glover must be made much higher than those of the Gay-Lussac tower, on account of its smaller height. This is far from a disadvantage, as the Glover tower must anyhow be placed at such a height that the burner-gas will have to rise a little in passing to it.

The acid-tanks are each provided with an outlet-valve *k* and a waste-pipe *l*; the former leads to the acid-distributor, the latter direct to the tower-cover *n*. This cover is, as seen best in fig. 227, suspended from joists *pp*, which lie across the beams *ff*; strong straps, nailed to both sides of the joists alternately (figs. 227 & 230), hold the cover fast. This (precisely like a chamber-top, on the edges, where it is burnt to the chamber-sides) is jammed between the beams *f* and joists *p*; but thence towards the centre it is dished out, so that any acid running onto it cannot run down the sides of the tower, but stands in the depression of the cover and runs into the interior of the tower through the hydraulic joint

of the man-hole, or through a small swan-neck pipe provided on purpose.

The *tower itself* is made of 14-lb. lead, its bottom of 35-lb. lead, the straps of 9-lb. lead. Its sides are suspended from the top and side joists, just like those of a chamber. Figs. 227 & 228 show clearly that the lead stands a little off the wood, which is of importance for the protection of both the wood and the lead. At the same time figure 229 shows how the sides are constructed. In order to avoid seams at the corners, where they would be weakest and where they could not be very well repaired on account of the uprights *cc*, two of the sides are made of two sheets of lead (1, 2, each, which are burnt together in the middle, and which reach round the corners, where the sheets 3 are burnt to them. The seams are best burnt outside (p. 360). All the side sheets reach down from the top to the bottom without any horizontal seams, and hang loosely within the saucer. The tower proper is 30 feet high and has a horizontal section of 9 feet by 9.

Sometimes even square or oblong towers are not made in this way, but are constructed in single drums, like the circular towers (*vide infra*), the higher one always resting on the bevelled-out edge of the lower one. This is especially done where the tower-lead is not fastened to the ordinary frame by straps, but is held together by iron rings or closely touching wooden frames, which offer resistance to the thrust of the lining and packing. Iron hoops, however, have the disadvantage of gradually cutting into the lead, and closely-touching wooden frames cause the lead to be wasted much more quickly (p. 342).

The bottom saucer is formed of two sheets of lead burnt together in the middle and turned up all round to a height of 12 inches. Since sheets of 35 lb. to the square foot cannot be burnt together in the usual manner, they are joined thus: they are placed close together, after having the edges cut off slantingly and scraped clean (fig. 233); into the rebate, *a*, thus formed, lead heated a good deal

Fig. 233.



beyond its melting-point is poured: the latter, before solidifying itself, fuses the margins of *a*; and this is further assisted by a red-hot iron, so that the whole unites into a solid mass.

Latterly the frame and the towers themselves have been made more and more substantial; for instance, towers are met with whose sides, up to the height of the gas-pipe, are of 25- to 30-lb. lead, and whose saucer is of 50- to 60-lb. lead.

Sometimes, as we have seen above, the bottom of the tower stands in another saucer, filled with water, which is allowed to get hot, but even in this state forms a protection of the inner saucer against overheating. In other cases there is a constant flow of cold water round the bottom saucer, so that the acid gets cooled to some extent before running away, which is an additional advantage.

The tower is now *lined* and at the same time provided with a *grating* (dome) for the packing. The lining must consist of the best hard-burnt, acid-resisting bricks that can be procured. Some bricks are not quite so suitable as others; for instance, the "blue" bricks of Mold, in Flintshire, are better adapted for this purpose than other bricks of a more refractory but less acid-resisting nature. Best of all, but more expensive, are bricks of stoneware or glass. The Aussig chemical works, the Bendorf works near Coblenz, and especially Ernst Boeing at Bad-Nauheim (see below) make very good lining-bricks for Glover towers. The lining is made 2 feet 3 inches thick at the bottom all round, as high as the grating, so that a clear space of 4 feet 5 inches remains open in the centre; the 1 inch remaining from a total section of 9 feet square is caused by not putting the lining close to the lead sides, but leaving a clear space of $\frac{1}{2}$ inch all round (see fig. 228). Immediately over the entrance-pipe *r* for the gas there are four semicircular arches, *ss*, as seen in fig. 227 in section, in fig. 228 from above. They are arched from the side lining, made very strong for this purpose, and serve both for carrying the lining and for dividing the current of gas. To avoid the side-pressure altogether, some manufacturers, instead of arches, construct a grating of fire-clay slabs, as shown in figs. 231 & 232; the former shows how a dwarf wall runs almost through the middle of the tower-bottom, carrying on its top (fig. 232) a number of slabs standing edgewise, 3 feet 3 inches long by 18 inches height and 6 inches thickness, which rest on this dwarf wall and upon the side walls. In any case the arches, if such are used, are levelled up to a plane surface at the top (fig. 227). (Walsh, E. P. 1486, of 1884) on the contrary makes the arch lancet-shaped for

better distribution of the gases, but very unnecessarily. The lining of the tower is now continued for a height of about 4 feet with a thickness of 18 inches, then for 8 feet with only 14 inches, and for the last 8 feet with only 9 inches thickness.

The whole lining of the tower as well as the dome (arch) must be walled *dry*, without any mortar of any kind. Tar mortar would melt; and fire-clay would be converted into aluminium sulphate. This happened at one of the first works on the Tyne at which the Glover tower was tried, where after a few weeks the lining lifted up the cover and rose above the tower. In order to make the arch sufficiently stable without any mortar, it should not be made of ordinary fire-bricks cut to shape, but of large fire-clay lumps expressly manufactured for the purpose, whose sides join smoothly together. In some works all the bricks of the lining are ground upon one another, so that only extremely small joints remain.

The bottom must be covered by 3-inch slabs of fire-clay, so that the hot gases and hot acid do not impinge upon it (this is, by mistake, not shown in fig. 227). It is even advisable to put a piece of lead loose on the real bottom, and to cover this again by the fire-clay slabs.

It is not considered bad work if the lining of a Glover tower stands for three years without having to be renewed.

The *packing* of Glover towers in England almost everywhere consists of flints, picked from the chalk and purified by washing with hydrochloric acid. This material is absolutely acid-resisting and does not fly by the heat; but it does not possess any great surface, and it is very heavy. For the latter reason in many places the upper third of the tower used to be filled with the very hardest of coke; but this has led to several accidents, by the coke taking fire when there was by chance no feed of acid on; there is also always some action of the acid on the coke, as shown pp. 160 and 519. Most factories have given it up again, but it is still in use here and there.

Sometimes the Glover towers are simply packed with bricks, set on edge, in open work, as in a Siemens's recuperator. These bricks should of course resist the action of the acid. Blue Welsh bricks are frequently employed, and even some descriptions of common bricks seem to stand very well (J. Soc. Chem. Ind. 1885, p. 33). But undoubtedly they are always acted upon more or less, and yield up iron and alumina to the Glover acid (see below).

Silica, in the form of quartz, is frequently employed; but some descriptions of it are very liable to cracking in course of time, and filling up the gas-channels to such an extent that the draught, and with it the yield, is enormously impaired (Bornträger, Chem. Ind. 1886, p. 108). In opposition to this, Herreshoff (E. P. 1886) employs nothing but pieces of quartz within the Glover tower. As these cannot be very well obtained in the regular shape for an ordinary lining, he keeps the lining a foot or so away from the side of the tower, and fills the space thus formed with quartz sand. He asserts that this sand is not washed out with time, but this seems to be too favourable a view.

For packing the towers even broken glass or stoneware seltzer-water bottles with their bottoms knocked out have been found useful. But one of the best materials for this purpose seems to be that supplied by Ernst Boeing, at Bad-Nauheim (Germany). It consists of almost pure silica, is burnt at the intensest white heat, cuts glass, and resists both any change of temperature and the prolonged attack of hot acids. Lining-bricks of this material cost £1 10s. per ton; for packing the towers short open cylinders are made about 5 or 6 inches long and 4 inches wide (at £3 10s. per ton), which are thrown in without any special building up.

The manufacture of acid-proof bricks for Glover towers, according to 'Thonindustrie-Zeitung,' 1890, p. 642, requires material rich in silica more than in alumina, of a dense, non-porous character. Some descriptions of clay which are almost free from iron and can be burned to a clinker can be used directly. Where no such clay is available an artificial porcelain-like mixture can be made with from 25 to 30 parts felspar, 25 to 30 best China-clay or other good fire-proof clay, and 40 to 50 parts quartz. It should be burnt to a clinker, and should not shrink too much in the process. The bricks are best covered with a glaze consisting of 54 parts quartz, 84 felspar, 35 ground chalk, and 26 ground China-clay.

The perforated plates, on Lunge and Rohrman's system, which have been described on pp. 380 & 549, are not very well adapted for packing a whole Glover tower; in the lower part the holes would be too quickly stopped up by flue-dust, and they would be liable to crack there as well. But they can be employed very well in the upper half of the tower, the lower half being packed with bricks set edgeways &c. This plan obviates an objection made to the Boeing cylinders, viz. that in consequence of their

comparatively large size the acid and the gases are not sufficiently brought into contact and the denitration is not very perfect.

Even when employing some other kind of packing than bricks (such as flints, cylinders, and the like) it is advisable to place just over the dome, first two courses of the same kind of bricks as serve for the lining pigeonholewise in order to divide the current of gas in a regular way. It is a matter of course that the packing must be done as systematically and carefully as that of the Gay-Lussac tower.

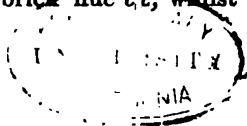
In some cases it is preferred not to fill the tower to its very top, viz. if the gas is cooled too much; for then even a part of the first-formed aqueous vapour might be condensed again to the liquid state, dilution thus counteracting the concentration. The temperature of the outgoing gas is generally about $60^{\circ}\text{C}.$; some manufacturers prefer from 60° to $75^{\circ}\text{C}.$ But if too much cooling must be avoided by leaving the upper portion of the tower empty, that portion might be left out altogether and the tower might be made so much lower. In fact, at some works in England towers of from 18 to 20 feet height are preferred to higher ones. This will, of course, depend upon the heat which the gas possesses when entering the tower, therefore upon the kind of ore burnt, upon the presence of dust-chambers, upon the length of way from the pyrites-burners to the tower, and so forth. According to numerous notes taken by me on this subject, the proper height for a Glover tower, under ordinary circumstances, seems to be from 26 to 30 feet. At one works, where two towers are erected, one of them 24 feet, the other one 36 feet high, it is found that the higher one does no more work than the lower one, so that the expense caused by the additional height, both in erecting and packing the tower, seems to have been thrown away.

The *gas* enters through the cast-iron pipe *r*, fig. 227, 2 feet 6 inches wide, and leaves the tower through the lead pipe *u*, 2 feet 3 inches wide. About the latter nothing need be said, except that on its bottom a small ledge *u*₁ is formed, which compels the acid squirted into it to run back into the tower; this pipe also usually rises a little towards the chamber. On the other hand, the fixing of the entrance-pipe *r*, which ought to have a little fall towards the tower, is not quite such a simple matter, and at first caused much difficulty. It is mostly made of cast iron, and has therefore in the great majority of acid-works, except in the above-mentioned cases,

a temperature of at least 300°C . The lead of the tower, where it touches the cast iron, will therefore be quickly wasted, and any kind of cement put between the two will not do much good; in most works a little gas was seen escaping at this joint, and it gave occasion for many repairs. The arrangement drawn in the diagram obviates this drawback. The pipe *r* here is not at all in contact with the lead, but with a metal casting, *v*. The latter is in the shape of a ring with two flanges perpendicular to the plane of the ring; the thickness of the metal is 1 inch, the clear space between the flanges 4 inches, the total height 8 inches, the inner diameter of the ring 2 feet $9\frac{1}{2}$ inches. Since the outside diameter of the pipe *r* is 2 feet $7\frac{1}{2}$ inches, there is a caulking-joint of 1 inch left free all round, which can be filled up with any hard cement—for instance, the ordinary rust cement made of iron filings, sulphur, and sal ammoniac; this cement can be rammed in hard, as it lies between two iron surfaces. In the side of the tower, in the place in question, there is a circular hole to whose circumference an upstanding flange is burnt, fitting the outer circumference of the ring *v*; between the lead and the iron a little ordinary tar and fire-clay cement is put; and a wrought-iron hoop in two parts with screw joints firmly binds together lead, cement, and cast iron. Since the outer part of *v* is cooled by the air circulating in the hollow space of the ring, only a small part of the heat can be communicated to it, which the inner part of the ring receives (already weakened by the layer of cement) from the pipe *r*; and therefore no difficulty is experienced in keeping the joint between lead and iron tight.

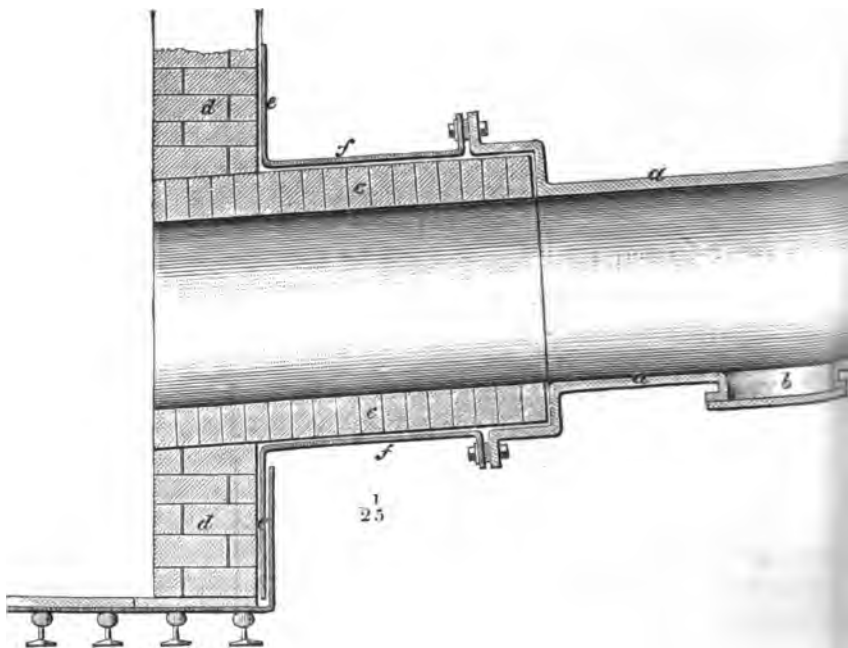
At the Aussig works the difficulty is obviated by attaching to the cast-iron gas-pipe coming from the burners a short piece of fire-clay pipe with a flange joint; the latter projects into the Glover tower; and the lead side of this is simply joined to the fire-clay pipe by a burnt-on flange surrounding the pipe, with cement between, and with an iron hoop pressing the lead flange onto the pipe. As the fire-clay pipe has much thicker walls, and is so much worse conductor for heat than a cast-iron one, this joint keeps tight even without the air-cooling just described.

The plan followed at Griesheim with perfect success is shown in fig. 234. The burner-pipe *a a* (which at *b* shows a cleaning-hole at the bottom) is enlarged at its end, so that it embraces one end of the dry-walled annular-shaped brick flue *c c*, whilst the other



end is tightly held in the brick lining *dd* of the tower. The lead side of the latter (*ee*) is continued into a lead cylinder (*ff*) surrounding the free portion of the flue *cc*; its end is bent round in

Fig. 234.



the shape of a flange, pressed against a flange of *aa* by means of an iron hoop and screw-bolts; and the joint is made tight by asbestos packing.

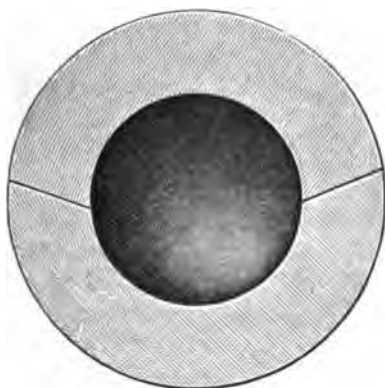
At some works the burner-gas is carried into the tower by means of pipes, made of Volvic lava, in two halves, as shown in fig. 235. In this case no special contrivance is required for protecting the lead at the joint.

Lastly, we must notice the "lip" *w*, fig. 227, where the lead side of the saucer is turned over to form a place for the acid to run off continually into a leaden spout. This part, over which hot acid is incessantly running, and which cannot remain covered by a protecting layer of lead sulphate, is exposed to very great wear and tear; and as it cannot well be repaired while the tower is at work,

the plumber must not neglect to put a false lip, consisting of a piece of sheet-lead beaten down close upon the real lip. The acid will then run over the false lip; and the latter, when worn out, can be replaced by a fresh piece in a few minutes' time.

Instead of a "lip," a lead tube of about $1\frac{1}{4}$ inch bore can be burnt in the side of the saucer, a little below its upper edge; but

Fig. 235.



the plumber must do this with the utmost care, and make the joint extremely strong, in order to save repairs, which can only be done by stopping the work. At Stolberg, where the Glover tower has no saucer, but the bottom and the sides are in one piece, there are no running-off pipes provided, so that one can work when the other is stopped up, &c.

For the *distribution of the acid*, formerly nearly everywhere reaction-wheels were used. They can be constructed of glass (p. 524); in England, however, they were usually made almost altogether of lead; this construction is shown on a larger scale in figs. 236 and 237. On a small wooden frame is a cast-iron plate *a*, perforated with holes in the centre and in twenty-four places not far from the circumference. It serves as a support for a lead cylinder *b*, of 2 feet 6 inches width and 12 inches high, whose bottom is divided into twenty-four compartments by radial ledges $1\frac{1}{4}$ inch high; in each of them there is a hole corresponding to one in the cast-iron plate; and lead tubes, *o o*, of $\frac{1}{2}$ inch bore, burnt to the lead of the cylinder, are carried thence

to the tower-cover, where the pipes are put loosely into short branches burnt to the cover, the joint being made with tar cement; figures 227 and 230 show the way in which the pipes are distributed. In the middle of the cylinder *b* (fig. 236) a smaller cylinder, *c* (7

Fig. 236.



Fig. 237.



inches wide), is burnt on, whose top is covered with a loose cap contracted in the centre. All these parts are fast. The movable parts consist, first, of an iron spindle, *e*, passing through the cast-metal plate *a*, and resting below with its steeled point on a piece of plate-glass *f*; on the top it is guided by an iron point screwed into an iron support, *g*; by turning the screw the spindle *e* can be made faster or slower. The upper part of *e* is surrounded by a thin lead tube; and at this part a dish, *h*, of thin lead is burnt on, from which the four tubes *i i* descend in the curve shown in both figures, so that the acid from the pipe *k*, when running out of *i i*, causes, by the reaction, the spindle *e* to rotate in the opposite direction, along with the parts fixed to it. Both acids, the nitrous vitriol and the chamber-acid, run into the lead dish *h*. The gas is prevented from escaping by small caps put on the mouths of the pipes *o o*, or in any other way. Exactly the same apparatus was used in the English works for the Gay-Lussac towers.

A much more perfect kind of acid-wheel, as constructed by Mr. Schaffner, is described and fully illustrated in our first edition, pp. 438 to 440. We abstain from repeating this here, since acid-wheels of any kind have become nearly obsolete now through the

introduction of the acid-spreading apparatus described on p. 526 *et seq.*, which is, of course, just as much used for Glover towers as for Gay-Lussac towers, hydrochloric-acid condensers, and so forth. There ought to be as many distributing-pipes as for the Gay-Lussac towers, that is, at least one for each superficial foot of the cover.

The regulation of the flow for the Glover tower is nearly always effected by hand, or else by the apparatus shown on p. 534. Any apparatus for an absolutely constant supply of liquid would be out of place here, as the relative quantities of nitrous vitriol and chamber-acid vary, and must be regulated according to the state of concentration and denitration of the outflowing acid.

According to the dimensions given above, it is seen that the *cubic contents of the Glover tower*, measured inside the lead, without taking any account of the lining, the space underneath the dome, &c., for a daily consumption of 9 tons pyrites with 48 per cent. sulphur, amounts to $9 \times 9 \times 30$ feet—that is, to 2430 cubic feet. This for every ton of sulphur put in daily amounts to about 550 cubic feet; and this number may be considered the proper one for the proportions of a Glover tower; and at some of the largest works it is closely approached. At the Saint Gobain Company's works the real working space (*i. e.* that occupied by the packing moistened with acid) is from 70 to 160 cubic feet per ton of pyrites, or say, twice as much per ton of sulphur; and as the proportion of the working space to the total space is not much more than 1 : 2, it may be said that the higher one of the Saint Gobain figures comes round to that which we have just stated as the normal one.

A Glover tower erected by Bode has been described and figured in detail by himself (prize essay, p. 60; Dingler's Journal, ccxxiii. p. 623); as in principle it offers no deviation from the above-described tower, only those matters will be mentioned in which there are divergences in detail. His tower is 7 feet 6 inches square and 25 feet high. The packing consists of broken pottery and, at the very top, of a little coke. For the acids there are sixteen inlet-pipes with two reaction-wheels. Bode (*l. c.*) also describes a floating reaction-wheel for very small pressure, which certainly is very perishable, being made of glass. He also describes a special contrivance for mixing the nitrous vitriol and the chamber-acid, which are supplied separately to the two reaction-wheels, imme-

diately after their entrance into the tower. Two branch pipes enter into a common hydraulic lute; and from these a bent pipe goes into the tower, which at the lowest part of the bend, where the two acids meet, has an outlet-hole. Such precautions, in most cases, are quite unnecessary; the acids can be mixed outside (see p. 594). Instead of a timber frame, such as is described above, in some places a cast-iron or even a wrought-iron frame has been employed with great advantage.

In lieu of the square section, at first universally employed for Glover towers, later on circular towers have come into use at many works. If lined with bricks, these are placed polygonally, unless suitable bricks, shaped to the proper bend, can be procured. In France they are usually lined with large blocks of Volvic lava, shaped to a circular section, and forming by themselves a sub-

Fig. 238.



stantial tower, although, of course, without any mortar, so that the lead shell is quite independent of them. Fig. 238 (from Frémy's 'Encyclopédie chimique,' t. v. section i. p. 188) gives a horizontal section of one of these circular towers which serves for

a set of chambers of 160,000 feet capacity, and is constructed as follows:—It has a width of 6 ft. 9 in. and 23 feet height, and rests on a block of masonry, set in cement, and protected on the top by an apron of 7 lb. lead. On this are erected eight uprights, *a, a*, mortised into octagonal horizontal frames at top and bottom. The uprights are 10 or 12 inches square, and are connected by two rows of cross-pieces, *b, b*, provided with iron binding-bolts. The holding-straps for the lead are attached to the uprights. The leaden shell consists of four drums which are burnt together in their places. The two first are 11 millimetres thick (=25 lb. lead), the third 8 mill. (=18 lb.), the fourth 6 mill. (=14 lb.). This last drum is dressed inwards at the top edge, to be joined to the cover, which is suspended by means of straps from five railway-bars resting on the top frame. Until the lead drums are in their place, only five of the eight upright posts are put in, so as to leave a passage. Each drum is bevelled a little outward on the top edge, so as to form a seat for the next higher one; the joint is then filled with molten lead. The drums, before fixing them, are left on the wooden cylinder on which they have been made, and are hoisted and lowered down into their place with the cylinder still in. The lava lining is provided for the first three drums only; the fourth is left naked, as the gases are here sufficiently cool not to injure the lead. There are 18 pieces of lava, *c, c*, six for each drum, in three courses with alternating joints, 10 or 12 inches thick. At Salindres they are 18 inches at the bottom, 12 inches in the middle, 8 inches at the top. The joints are made as thin as possible. The grate is formed by four or five sleepers made of lava, *d, d*, as shown in the drawing; they are sometimes supported in the centre by a thin wall, *e*.

The advantage claimed for circular Glover towers is that they require less lead for a given cubic space and that the lead suffers less than when it is bent in sharp corners. But while for Gay-Lussac towers these reasons may be accepted, they seem, in the case of Glover towers, to be more than counterbalanced by the much greater trouble and expense of constructing the circular lining.

Volvic lava can be obtained from several firms, *e. g.* Brosseau Lafilichat frères at Volvic (Puy-de-Dôme). In 1880 the cubic metre cost 60 francs; the lining of a large Glover tower as described cost 4500 francs (say £180).

At most works, quite properly, the Gay-Lussac and Glover towers are erected side by side, so that their tops are accessible by a common staircase, are even on the same level (in which case the Glover towers, being much lower, must stand on a higher foundation than the Gay-Lussac towers). It is unnecessary to point out how much the supervision of the work, the feeding of the towers, &c. is simplified by this plan. The position of the Glover towers being given, between the burners and the first chamber, it follows that the Gay-Lussac is at the greatest possible distance from the last chamber with which it is connected; but this is all the better, as the gases have more time to cool and get dried in the long connecting-pipe. It is also an advantage that the nitrous vitriol has not to run very far, as it sometimes contains gas (NO) which impedes its free running. As a long pipe increases the friction of the gaseous current, it mostly involves providing chimney draught for the chambers, which is certainly the best plan for all reasons (p. 427).

Working of the Glover Tower.—The Glover tower may operate with only the nitrous vitriol itself running down in it, without any chamber-acid; but in that case it does not deprive it of all the nitrous compounds, but of the principal part only (down to about 0.2 per cent. of N_2O_3), and at the same time concentrates it to 152°Tw . This acid may now be used again in the Gay-Lussac tower for absorption; and thus a circulation of acid may take place between the two towers. There is in this process always a certain addition to the acid, as within the Glover tower itself, by the action of the sulphur dioxide on the nitrosulphonic acid, free sulphuric acid is formed, as shown by the formula, p. 575.

However, the Glover tower is not usually fed (in the way just mentioned) with nitrous vitriol alone, except in the case of temporary disturbances. The apparatus is mostly so arranged as to be fed with nitrous vitriol (or with fresh nitric acid) and chamber-acid *together*, in which case not only is the denitration completed, owing to the initial dilution, but a very acceptable secondary effect is obtained, viz. concentrating the chamber-acid up to 152°Tw ., and depriving it also of the minute proportion of nitre which it generally contains. If the acid is not, as it is usual in England, brought in the chambers themselves to 116° – 124° , but only to 106°Tw ., it can for all that be concentrated to 141° without any difficulty in the Glover tower, even when the gas comes from a

shelf-burner for pyrites smalls and has therefore to be somewhat cooled in dust-chambers, on the supposition that the tower is placed close to the burners. This is done, for instance, at the Aussig works in Bohemia. That the denitration by sulphurous acid becomes more perfect by dilution, is a matter of course, according to the above-quoted researches of R. Weber, Cl. Winkler, and my own (p. 152 *et seq.*).

Where the leading-chamber is worked very strong, as described on p. 457, the Glover tower produces too strong an acid, which is incompletely denitrated and would injure the stability of the tower unless in this case a little water is run down at the same time.

The stream of nitrous vitriol and that of chamber-acid are regulated entirely according to the degree of denitration and of concentration shown by the acid running off at the bottom of the Glover tower. The more chamber-acid is run through (that is to say, the greater the dilution), the easier will be a full denitration; the less chamber-acid is used, the more concentrated will the acid arrive below. There is, however, no difficulty in attaining *both* objects, viz. to get an acid at the same time completely denitrated and testing 152° Tw., if good pyrites be burnt, and if the burner-gas be employed as hot as possible, say 300° C. and upwards, by placing the tower close to the burners. In the case of poor ores, or of smalls-burners with large dust-chambers, the denitrating action will also be complete; but the concentration cannot then be carried so far.

If it be assumed that the Gay-Lussac tower receives a quantity of acid equal to the total daily production, there will, of course, be just the same quantity of SO_4H_2 running down the Glover tower in the shape of chamber-acid, along with the nitrous vitriol, and therefore, according to bulk and weight, a little more of the chamber-acid, as this is more diluted. If the chamber-acid is on an average $=123^{\circ}$ Tw., equal to 70 per cent. SO_4H_2 (it may be safely brought up to this strength, precisely because the nitre dissolved in chamber-acid, when rather strong, will be expelled and utilized in the Glover tower), 117 parts by weight of the same correspond to 100 parts by weight of an acid of 152° Tw., $=81\cdot7$ per cent. SO_4H_2 ; or 100 vols. of the latter are equal to 128 vols. of the 123° acid, and the latter would be the proportion in which the two acids are mixed. The result would be a mixture of acids

of 136° Tw. entering the Glover tower at the top, which can be fully denitrated by sulphurous acid, especially when hot. If less Gay-Lussac acid has been used than the above, the mixture of acids entering the Glover tower will show a lower specific gravity than 136° Tw., and will be all the more easily denitrated.

During the first years of the working of the Glover tower it was generally assumed that the acids must only be mixed *inside the tower*, because during their mixture nitric oxide would be given off (comp. p. 590). On this principle was founded the mixing-apparatus described by me in my first publication on the Glover tower (in Dinger's Journal, cci. p. 348), and the distributing-wheels with double outlet and separate distributing-chambers and pipes. But it follows from the calculation just made that a mixture of equal parts of acids, when chamber-acid of 123° Tw. is used and the daily make of acid is passed through the Gay-Lussac tower once a day, would be equal to 136° Tw. In an acid of this strength nitrososulphuric acid is sufficiently stable, at least at the ordinary temperature; and it is possible, and has been done in many places for years past, to mix the two acids before they enter the Glover tower, which greatly simplifies the distributing-apparatus. Even when only one half of the total daily make of acid is used for absorbing, the mixture of this with the total chamber-acid still comes to 131° Tw., which is equally a safe strength. If, however, the conditions are more unfavourable in this respect, the dilution can no longer take place outside the tower. If, for instance, the chamber-acid is only 106° Tw. strong, 131 parts by weight of it correspond to 100 parts of acid of 152°; and if of the latter only half the equivalent is taken (that is to say, 100 parts by weight of acid of 152° Tw. to 262 parts of 106°), the density of the mixture only comes to 118°, at which strength nitric oxide begins to escape from a solution pretty rich in nitrososulphuric acid; but the above is an extreme case which will rarely happen.

In these calculations the degree of saturation of the vitriol with nitrous compounds is not yet taken into account; the less the amount of acid used every day in the Gay-Lussac tower, the more will it be saturated with nitre, and there will be more danger of gas escaping from the nitrous vitriol when mixing it with chamber-acid.

The temperature of the acid running off from the Glover tower is usually between 120° and 130° C. If the work is very much

pushed, it may reach 140° or even 150° . In the few works where this happens, no bad consequences have been observed; but in one works I was told that a little more nitre was always used whenever the acid became hotter than 138° C. Still the observations made there were not sufficient to establish this result as certain, if all disturbing conditions be eliminated. The gas leaving the tower at the top has generally a temperature of from 50° to 80° C.; it should not be above 60° , at which temperature cooling it before it enters the chambers is quite unnecessary.

One of Bode's towers, working with dust-burners, had to receive the burner-gas after passing through a large dust-chamber. The gas, therefore, only reached the tower 152° to 180° C. hot; and the temperature on leaving it varied between 30° and 40° C. The hot acid running off showed between 96° and 110° C. When this tower was only employed for concentrating chamber-acid, it daily evaporated 6 tons of water and produced 2 tons $3\frac{1}{2}$ cwt. acid of 144° Tw. from chamber-acid of 110° . This corresponds to a saving of coals for chamber-steam equal to $1\frac{1}{2}$ cwt. per diem. When the tower was employed both for concentrating and denitrating, it supplied daily on an average 2 tons of acid of 144° Tw., and evaporated 9 cwt. of water; the denitration was perfect. The kiln-gas had $7\frac{1}{2}$ per cent. by volume of sulphur dioxide. Of course the above results are much less favourable than with the usual initial temperature of 300° to 400° C. Even in the latter case the temperature of the gas leaving the tower does not exceed 50° to 60° C. Such a hotter tower of 8.28 square metres section, according to Vorster ('Dingler's Journal,' ccxiii. p. 411), in twenty-four hours evaporated 1400 kilog. water; another tower of 4.55 square metres section, 1048 kilog. water, the kiln-gas containing 8 per cent. by volume of sulphurous acid.

According to Wunderlich (Zeitschr. f. d. chemische Grossgewerbe, i. p. 74) and Bräuning (*l. c.* p. 140), Glover towers do not seem to offer any advantage when the temperature of the kiln-gas on entering is below 200° C.; this is the experience of the Oker smelting-works. There each Glover tower, 5 feet 8 inches square and 17 feet 3 inches high, concentrates daily 6 tons 2 cwt. of acid to 144° Tw., but only when pyrites is used; with lead matt and the like the initial temperature of the gas sinks to 230° , and the quantity of acid concentrated to 3 tons of 144° Tw.

Even when in Bode's Glover tower, by an accident, the percent-

age of the kiln-gas had sunk down to 6 or 5 per cent. of sulphur dioxide, there was still complete denitration and an evaporation of 7 cwt. of water daily, equal to 1.7 ton of acid of 144° Tw. Bode calculates from this that, even when calcining the poorest ores, the Glover tower still remains a useful apparatus.

Hasenclever reports (Ber. d. deutsch. chem. Gesellsch. 1872, p. 506) that the Glover tower had been successful in combination with his plate-burners; I have found the same in combination with Malétra's or other shelf-burners in a large number of works, at all of which, of course, there were dust-chambers.

At those works where sulphuric acid is made from *brimstone*, Glover towers are not so regularly found as with *pyrites*-burners. The reason of this cannot be insufficient heat of the gases, as is proved by the practice of several large works where the Glover towers work perfectly well with *brimstone*-burners, and shows all the advantages found elsewhere. Sometimes it is asserted that the higher value of *brimstone* acid as against *pyrites* acid is impaired by iron carried into it from the Glover tower; but this cannot take place except with an inferior description of packing material, and it is entirely avoided by confining the work of the tower to denitrating the nitrous vitriol, and taking the sale-acid from the chambers or from lead pans put over the burners (Chap. XI.). The real reason for the comparative neglect of the Glover tower at *brimstone*-acid works is this, that many of these works are of small extent and cheaply laid out, and are managed with insufficient care, so that their owners would rather lose nitre and sulphur than incur the expense of erecting and the trouble of working Glover towers. At several large American works I found Glover towers working most satisfactorily with *brimstone*-burners. In these cases the heat of the gases was first utilized for concentrating chamber-acid up to 140° Tw. or even (in H. Glover's sulphur-burner, p. 201) to 168° Tw., after which the gases entered the Glover tower and there produced acid of 150° Tw., with a temperature of from 126° to 130° C., sufficient in quantity for amply supplying the Gay-Lussac tower.

At larger works, possessing a number of Glover towers, it is a frequent and convenient arrangement to work them in different ways, viz., partly for making acid for the Gay-Lussac towers and partly for decomposing acids. The first should be as strong as possible, and need not be entirely denitrated; it can be obtained

in this state by feeding but little chamber-acid along with the nitrous vitriol. There is thus a constant interchange of acids between the two kinds of towers; but the Glover tower makes a good deal of fresh acid, so that part of it must at all events be employed for other purposes.

The acid for decomposing salt, or for sale, &c., on the other hand, should be entirely denitrated, and need not be so strong as the former; for this purpose much more chamber-acid is fed along with the nitrous vitriol.

We have already (p. 575) pointed out the *various functions* which are fulfilled by the Glover tower. The object for which it was first constructed, the *denitration of the nitrous vitriol*, that is the recovery of the "nitre" from this and the restoration of it to the chambers, is carried out by its means in the most perfect way and without any trouble. It is easy to work it so that the acid at the bottom contains even a slight excess of SO_2 (which is compatible with a very slight percentage of N_2O_5); nor is there any very high temperature required for it, especially when the nitrous vitriol is diluted with chamber-acid. In fact at some works the heat of the pyrites-kilns or the sulphur-burners is previously utilized for concentrating the acid, and the gases only then enter into the tower, where they perform the work of denitration, together with some little concentration, and are cooled down to the proper temperature for entering into the chambers. This plan is especially recommended for works where much acid is sold or is further concentrated to "rectified oil of vitriol," for which purpose the acid concentrated in the Glover tower is too impure (see below). This case also arises when burning arsenical ores, where the gases, in order to deposit the large quantity of flue-dust, have to pass very long channels (p. 300 *et seq.*).

That the fear of losing any nitre in the Glover tower by reduction to nitrous oxide or nitrogen is totally unfounded, has been proved before (p. 571 *et seq.*). Far less nitre is consumed in the manufacture of vitriol than before the introduction of the Glover tower; and the change has in most cases been so sudden, that it seems impossible to overlook this evidence.

The second principal function of the Glover tower is that of *concentrating* chamber-acid, which is intimately connected with two other functions: *cooling the gases* and *supplying part of the steam* for the chambers. The concentrating action of the Glover

tower was first studied in detail by Vorster ('Dingler's Journal,' ccxiii. p. 413), but his paper is useless, as he entirely neglects the acid brought over with the burning-gas as SO_3 and that formed within the tower itself. Both these sources have been taken into account in the investigation of Scheurer-Kestner (Bull. Soc. Chem. xliv. p. 98). From his analyses of burner-gases it appeared that these contained up to 9 parts of SO_3 to 100 SO_2 ; the average was about 3.5 parts. As there is enough water even in the air and the pyrites to hydrate the SO_3 , it is sure to be retained in the Glover tower. He further shows the mistakes committed by Vorster in his calculations, from which the latter had concluded that very little acid was newly formed in the tower; and he opposes to this not merely the practical experience, according to which the introduction of a Glover tower saves from 10 to 20 per cent. of chamber-space, but also some special large-scale experiments made with an actual tower at the Thann acid-works, by carefully measuring for some weeks the excess of acid coming out from the tower over that going in. Thus it was found that the Glover towers made 15.7 to 16.3 per cent. of all the acid produced in the manufacturing apparatus. To this should be added the acid volatilized or mechanically carried away from the towers into the chambers, which was (only partially) estimated by measuring that which condensed in the connecting-pipes, and which amounted to 2 or $2\frac{1}{2}$ per cent. of the total make, bringing the action of the towers to 17 or 19 per cent. This was entirely proved by the result of prolonged working on the large scale; for the same set of chambers which had previously made 6 tons of O.V. in 24 hours, made 7.28 tons, or 17.5 per cent. more, after adding a Glover tower to the apparatus.

Hence the concentration observed in the Glover tower is to a great extent only an apparent one; it is not merely due to volatilization of water, although this also takes place to a considerable extent, but also to the formation of very much H_2SO_4 , which dissolves in the acid used for feeding and raises its strength.

In a previously quoted paper (Bull. de la Soc. Ind. de Mulhouse, 1889, p. 267; abstracted by me in Zeitschr. f. angew. Chem. 1889, p. 275) Sorel has tried to follow the functions of a Glover tower, so far as they refer to the new formation of sulphuric acid, by elaborate calculations. We must omit the greatest part of these, as he at the outset commits several grave errors which

modify some of his figures to the extent of four or five times the real values. This refers especially to Sorel's calculation of the number of times the nitrous gases enter into reaction during their passage through the Glover tower, and the time occupied by each such reaction; we shall, therefore, substitute for these a new calculation, based on the figures given on p. 470, indicating the real quantities of nitre supplied to the tower in one shape or another at a well-managed works. We may assume that for each 100 parts of sulphur burnt in 24 hours there is in ordinary cases supplied to the chambers the equivalent of 10.25 parts of commercial nitrate, of which about $\frac{7}{8}=7.32$ parts are in the shape of nitrous vitriol, and $\frac{3}{8}=2.93$ parts in that of fresh nitric acid. These would yield the following quantities of oxygen for each ton, say 1000 kilog., of sulphur burnt, on being reduced to nitric oxide:

73.2 kil. 96 per cent. nitrate as

$$\text{nitrous vitriol yield } \frac{73.2 \times 8 \times 0.96}{85} = 6.61 \text{ kil. oxygen.}$$

$$29.3 \text{ kil. ditto as nitric acid yield } \frac{29.3 \times 24 \times 9.6}{85} = 7.82 \quad ,,$$

$$\text{Total } 14.43 \quad ,,$$

Now each 16 parts of oxygen oxidize 32 parts of sulphur, entering the tower in the shape of SO_2 , to H_2SO_4 . Hence the above 14.43 kil. of nitric oxygen will produce sulphuric acid from 28.83 of sulphur, if its action is exerted only once. In reality, however, up to 250 of the total 1000 S are converted into H_2SO_4 within the tower, which certainly includes the SO_3 carried over from the kilns; but as this on an average does not exceed 3.5 per cent. of the total S, we shall be safe in assuming that 200 kil. S, as SO_3 , are actually oxidized within the tower, so that $200 - 28.8 = 171.2$ kil. of S have been oxidized by renewed action of the nitrous gases. Considering further that the nitric acid is reduced to NO, and that in the further reactions this transfers upon SO_2 only as much oxygen as its equivalent of nitrous vitriol, the total oxygen transferable by each single action of the nitre present is only $6.61 + 2.21 = 8.82$ kil., equivalent to forming sulphuric acid from 17.64 kil. sulphur. There must, hence, have been $\frac{171.2}{17.64}$, or, roundly speaking, *ten subsequent transfers of oxygen* upon SO_2 within the Glover tower after the first action of the nitre introduced.

We can also calculate the time occupied by each such transfer. The cubic contents of an ordinary Glover tower, counting the space within the lining from the surface of the grate to the top, varies from 180 to at most 300 cubic feet per ton of sulphur burnt in 24 hours. If we take the very usual capacity of 200 cubic feet, and deduct 50 per cent. for the packing of flints, &c. (which is probably below the truth), and if we further assume that the denitration is practically complete halfway down the tower (which is decidedly allowable), we get $\frac{200}{4} = 50$ cubic feet as the real empty space

within which the acid-forming reactions take place, or slightly under 1.5 cubic metre. Now the volume of gases given off by the combustion of 1000 kil. of pyrites-sulphur in a properly conducted operation is, as shown on p. 312, about 8144 cubic metres, calculated for 0° and 760 millim. pressure. From this we must make a slight deduction for the gases taken out by the formation of H_2SO_4 , say, up to the middle of the denitrating zone, equal to $\frac{1}{10}$ of the total $\text{SO}_2 = 70$ cubic metres, and the corresponding quantity of oxygen, equal to 35 cubic metres, leaving 8039 cubic metres at 0° and 760 millim. pressure, or, roundly, 8000 cubic metres. As the average temperature of the denitrating zone is about 90° C., the above quantity of gases in reality occupies a space of about 10,700 cubic metres, or $\frac{10,700}{1.5} = 7107$ times the

active space, that is the denitrating zone, of the Glover tower. Hence the sojourn of the gases within that space is $\frac{24 \times 60 \times 60}{7107}$, or as

nearly as possible 12 seconds. But we have seen that there are eleven successive actions of the nitrous gases upon SO_2 within the tower, so that each of these, consisting, according to the older theories, of an oxidation and a reduction, or, according to the modern theory to be developed in the next chapter, of the formation and decomposition of nitrososulphuric acid, cannot require much more time than one second.

We may draw another important inference from the established facts. The usual allowance of chamber-space per lb. of sulphur burnt in 24 hours is 20 cubic feet, or 44,800 cubic feet per ton of sulphur. Of this ton, one fifth is oxidized into sulphuric acid in the Glover tower, leaving four fifths for the chambers. This means that 50 cubic feet of active Glover-tower space, as defined above, make acid from 0.2 ton of sulphur, or 1 ton of sulphur

=250 cubic feet, whilst 44,800 cubic feet of chamber-space make acid from 0·8 ton of sulphur, or 1 ton=56,000 cubic feet. In other words: *the denitrating zone of the Glover tower makes 224 times more acid than an equal cube of chamber-space.* If we take the minimum chamber-space allowed at English or German alkali-works, viz., 16 cubic feet per lb. of sulphur=35,840 cubic feet per ton, this still means 44,800 cubic feet for the acid really made within the chambers, or only $\frac{1}{125}$ of the activity of the Glover tower*.

We shall now better understand why I recommend replacing a large portion of the chamber-space by columns acting in a similarly energetic way as Glover towers (Chap. VI. p. 380 *et seq.*).

This enormous action of the Glover tower is explicable on the assumption that the nitric oxide set free in the lower parts of the denitrating zone, according to the equation



is fixed again in the upper parts by the reaction:



the nitrososulphuric acid, thus re-formed, on descending into the lower regions, is denitrated again, and the NO, thus flying backwards and forwards, incessantly and quickly transfers oxygen upon the sulphurous acid arriving in the shape of burner-gas. This action, which, of course, equally takes place in the chambers, is in the Glover tower immensely aided by the continuous mixture of the gases and their constant shocks against surfaces wetted with nitrous vitriol. The very large amount of heat produced by the chemical reactions cannot give rise to any considerable elevation of temperature, as the heat is expended in evaporating water from the acid tricking down, and concentrating this acid, as pointed out before.

If the tower be too high, and if the top be kept too cool (which will by itself follow from the former), much less than the above calculated work will be done in it. In this case there will be a considerable condensation of the steam, generated below, in the upper region of the tower; this will facilitate the denitration near the top itself, and the NO here generated will be carried over into the chamber without performing the above-described multiple work. Experience has indeed shown long ago that Glover towers ought not to exceed a certain height (25 or at most 30 feet) to do the best possible work, both for evaporation and for forming new

* These calculations are more correct than those I have given in the *Zeitschr. f. angew. Chem.* 1889, p. 388, on the basis of Sorel's somewhat doubtful data and together wrong calculations.

acid. But Sorel, in my opinion, goes very much too far in advising that the Glover towers should be kept as hot as possible, and should be fed with as concentrated an acid as possible. He looks only at one side of the matter, and that decidedly the less important one, viz., that there should be as great a production of acid as possible within the Glover tower, by retaining the nitrous compounds within it a very long time. He neglects two other considerations of much greater importance: that by his mode of conducting the process the *denitrating* work is greatly impaired, so that the acid issuing at the bottom carries away very sensible quantities of nitre, and that by the great heat of the gases and the concentration of the acid the life of the tower is very much shortened. Sorel's plan interferes both with the complete denitration of the nitrous vitriol, and also with the well-known utility of the Glover tower for bringing the chamber-acid just up to the strength required for decomposing salt, &c. (say, 140° to 145° Tr.), merely in order to force rather more SO_2 through the chambers than they can otherwise manage to oxidize; but this object does not seem worth incurring the serious drawbacks just named.

The following *drawbacks* are connected with the Glover tower, the first of which is, however, only temporary, and much less felt where there is no coke-packing in the Glover, but only in the Gay-Lussac tower. This coke communicates to the acid, especially at the beginning, a brown colour (due to organic substances), which is quite immaterial to its technical application, but injures its sale. After a little time this ceases; and the acid running away from the Glover tower is then as clear as water, and, on account of its strong refraction of light and oily appearance, is compared by the workmen to "whisky."

The contamination with iron is permanent, and is somewhat stronger than in acid made from the same pyrites in ordinary chambers, precisely because the tower at the same time serves for keeping back the flue-dust. Anyhow this contamination will amount to less than in acid made from pyrites-dust in Gerstenhöfer's burner (Bode). According to Hasenclever, his Glover-tower acid contains 0.05 per cent. of iron (Berl. Ber. 1872, p. 506).

Besides iron, the Glover-tower acid frequently contains considerable quantities of alumina, of course in proportion to the resistance of the lining and packing material to the action of the acid.

The quantity of flue-dust and of the sulphates of iron and

alumina formed within the tower are often so considerable that the tower cannot be worked for a considerable time without washing it down from time to time by a strong jet of water. But in the long run this is not sufficient; the interstices get filled up with hard crusts, and the tower must be stopped for re-packing, which is a very troublesome and expensive operation. It is hence advisable to go to some extra expense for the best obtainable lining and packing material.

An interesting application of the Glover tower is that for utilizing the nitrogen acids remaining in the acid from the manufacture of nitrobenzene and nitroglycerine; these are used in some works for running down in the Glover tower.

Where the Glover-tower acid is only used, apart from the service of the Gay-Lussac tower, for decomposing salt, for manufacturing manure, and for many other purposes, its impurities are of no consequence. But it cannot be used for such purposes where those impurities would be troublesome, and especially not for higher concentration to "rectified O.V." in glass or platinum retorts, as then hard adhering crusts of ferric sulphate are formed. Even then the use of a Glover tower need not be renounced, but it must be either treated only as a denitrator, the heat of the burner-gases being *previously* utilized for concentrating acid (*comp.* p. 201 & 228, and Chap. XI.); or else the acid required for the manufacture of rectified O.V. and similar purposes is taken out of the first chamber without passing it through the tower.

Denitration by other means.

The proposal of Garroway (E. P. 1673, of 1883) to effect the denitration and concentration of the acid without a Glover tower, by means of stoneware vessels placed in the gas-flue between the burners and the first chamber, seems to offer very little prospect of success.

Windus (E. P. 367, 1882) proposes, in lieu of denitrating the nitrous vitriol in Glover towers, to do this by agitating it within the chambers, and promoting the disengagement of the gases by producing a vacuum. The agitation is to be produced by mechanical means, or by allowing thin jets of acid to fall into the acid at the bottom of the chamber. It is unnecessary to point out the impossibility of denitration by this procedure.

CHAPTER IX.

THEORY OF THE FORMATION OF SULPHURIC ACID IN THE
LEAD CHAMBERS.

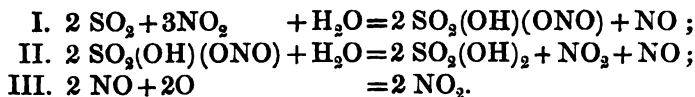
WHEN describing in previous Chapters the behaviour of sulphurous acid towards the various nitrogen compounds in the presence of water, sulphuric acid, &c., and the formation and decomposition of nitrososulphuric acid, we have been obliged repeatedly to forestall theoretical considerations; but these will now be brought forward connectedly and in detail.

We must from the commencement bear in mind the fact that during the burning of sulphur, whether in the form of brimstone or pyrites, substantially sulphur dioxide (SO_2) alone is formed; the formation of sulphuric anhydride or acid, always occurring at the same time (at least in the case of pyrites), is not taken into account here, being merely a secondary reaction, and not exempting us from the task of explaining the oxidation of the sulphurous acid in the lead chambers. That this does not take place to an appreciable extent by the direct action of the atmospheric oxygen, may at the outset be taken as established. But it is just as certain that the oxygen of the nitre introduced into the process does not suffice to account for it; for the sulphurous acid from 100 parts of sulphur requires another 50 parts of oxygen in order to be oxidized to sulphuric acid, which would correspond to 88.5 parts of nitrate of soda, even if this compound were reduced to nitrogen. But it is well known that, under favourable conditions, only $\frac{1}{30}$ to $\frac{1}{25}$ of the above quantity of nitre is used; and this fact must now be explained.

The first theory on this subject was propounded as early as 1806, by Clément and Désormes ('Annales de Chimie,' lix. p. 329); and it must be owned that they had observed most of the essential facts, and connected them by a theory which has not had to be

entirely abolished, but only to be modified with the growth of our knowledge. They had studied the behaviour of sulphurous acid towards a mixture of nitric acid and atmospheric air; and they proved that, even in the crude process then in use (where a mixture of brimstone, saltpetre, and moist clay was heated in a furnace and the gaseous products were conducted into the lead chamber), considerably more oxygen was transferred to the sulphurous acid than the saltpetre contained. They already explained this fact in substantially the same way as it is explained now-a-days, viz. thus:—From the nitre-gas oxidized by atmospheric oxygen, and from the sulphurous acid, sulphuric acid is generated, whilst the nitre-gas is re-formed. The nitric acid is only the instrument for the complete oxidation of the sulphur, which in doing its work is not destroyed; for its “basis,” the nitre-gas takes up oxygen from the atmospheric air in order to present it to the sulphurous acid in a suitable state; but it remains in its original state at the end of the process of forming the sulphuric acid. The presence of water they explain as necessary, first, for keeping the temperature of the reaction sufficiently low; secondly, for condensing the sulphuric acid as it forms. They also observed in the process the production of white star-shaped crystals, which on contact with water gave out nitre-gas with a strong evolution of heat, and they already suspected that this compound had an essential share in the acid-forming process.

H. Davy showed, in 1812, that the presence of water is absolutely necessary (Berzelius, ‘Lehrbuch,’ i. p. 471), because in the dry state the gases do not react upon each other; but a small quantity of water added to the mixture of sulphur dioxide and nitrous vapours causes the formation of the crystals observed by Clément and Désormes. Davy, therefore, considered that body an intermediate link indispensable for the formation of sulphuric acid; with our present notation we should express his opinion in this way:—

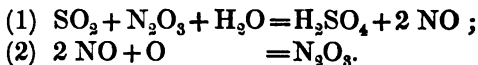


Therefore we commence with 3 NO₂; and we recover of this 1 NO₂ in the equation II., 2 NO₂ in the equation III., in order to begin the process over again.

This opinion has been accepted by many other chemists, for instance La Prévostaye (Ann. de Chim. et de Phys. lxxiii. p. 326) Gmelin also adopts it; he says ('Handbuch,' 5th ed. i. p. 875):—"In all these cases there are mixed in the chamber sulphurous acid gas, vapour of hyponitric acid, arising from the nitric-oxide gas and from the oxygen of the air, and aqueous vapour, which is introduced on purpose. There is a crystalline compound of sulphate of nitric oxide with oil of vitriol formed, which sinks down to the bottom of the lead chamber in the shape of a thick white mist and dissolves in the water present there and forms dilute sulphuric acid, nitric-oxide gas being evolved. This nitric-oxide gas, with the remaining oxygen of the air, again forms vapour of hyponitric acid, which condenses a fresh quantity of sulphurous acid gas into the crystalline compound, and so forth."

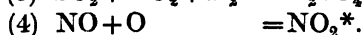
An *apparently* simpler explanation of the vitriol-chamber process was given by Berzelius ('Lehrbuch der Chemie,' Woehler's translation, 4th ed. 1835, vol. ii. p. 12). He believes the formation of chamber-crystals to be not a necessary intermediate process, but only an exceptional case happening in some parts of the chamber where steam is wanting. The process proper, according to him, consists of the transference of oxygen from "nitrous acid" to sulphur dioxide (and water), producing sulphuric acid and nitric oxide, from which, by means of oxygen, nitrous acid is regenerated.

We should therefore have to express the process in our present notation by the following equations:—



But I have shown (Ber. d. deutsch. chem. Ges. 1888. p. 3225) that Berzelius, as was natural in those days, made no sharp distinction between N_2O_3 and N_2O_4 , and evidently by "nitrous acid" often means N_2O_4 . It is also an important fact that in his 'Jahresbericht' for 1844, when the difference between N_2O_3 and N_2O_4 had become clearer, he distinctly states (p. 62) that N_2O_4 is formed when NO meets a sufficient quantity of oxygen or atmospheric air, whilst with an excess of NO, that is, in case of a deficiency of oxygen, N_2O_3 is formed, together with some N_2O_4 . In fact most subsequent writers have not introduced nitrous anhydride, but *nitrogen peroxide* into the explanation of

the chamber process, starting from the indubitable fact that in ordinary laboratory experiments nitric oxide with an excess of oxygen forms almost entirely, or perhaps even exclusively, nitrogen peroxide, and tacitly assuming (without any proof of ever having attempted to detect its presence) that nitrogen peroxide was the oxide of nitrogen prevailing in vitriol-chambers; also overlooking that the above-mentioned laboratory fact is entirely modified by the presence of other substances in the vitriol-chamber. Thus it came to pass that the following equations were very generally held to express the vitriol-chamber process:—



The great simplicity of this expression seemed to be its recommendation, but it was overlooked that in nature the simplest explanation is very often *not* the expression of truth.

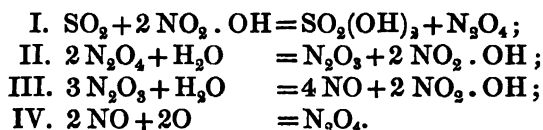
Even long after Berzelius no sharp distinction was made between the equations (1) + (2) and (3) + (4); probably most chemists tacitly assumed, as was explicitly done by some, that the vitriol-chambers contained a mixture of N_2O_3 and N_2O_4 , both of which acted as oxygen carriers upon SO_2 , and this was generally meant when speaking of the "theory of Berzelius," which was certainly accepted by very many chemists.

For some time another theory, that of Peligot, published in 1844 (*Annales de Chim. et de Phys.* (3) xii. p. 263), contested the palm with it, and was accepted, more especially in France, until very recently; even Kolb (*Études sur la fabrication de l'acide sulfurique*, Lille, 1865, p. 22) adhered to it; and so did Pelouze and Frémy (*Traité de Chimie*, 2nd edition, i. p. 398).

Peligot, like Berzelius, denied that the chamber-crystals had an essential share in the formation of sulphuric acid, or that they appeared at all in the regular process, either in a solid form or in solution. He attributes the oxidation of the sulphurous acid within the lead chamber exclusively to nitric acid, not to the lower oxides of nitrogen. The water is added to decompose the hyp-nitric acid formed from nitric oxide and atmospheric oxygen, or the nitrous acid formed at the same time, into nitric oxide and

* Here, as everywhere else, we shall use the symbols N_2O_4 and NO_2 as interchangeable according to convenience of expression.

[hydrated] nitric acid, and thus to regenerate the only oxidizing agent acting in this process, viz. nitric acid. In watery solution, he says, no nitrous acid exists [which is altogether wrong]; from a mixture of nitric oxide and atmospheric air not N_2O_3 , but only N_2O_4 is formed. These opinions will be made clearer by the following equations (translated into modern symbols) :—



The experiments upon which Peligot founded his theory certainly proved that *concentrated* nitric acid oxidizes sulphur dioxide even at the ordinary temperature, nitrogen peroxide being formed. But sulphur dioxide acts with more difficulty on dilute nitric acid, and only with the aid of heat, nitric oxide being formed. Weber points out that Peligot's experiments do *not* prove that nitric acid of that degree of dilution which, according to his own theory, must exist in the lead chambers, at the temperature prevailing there, is really decomposed by sulphurous acid. On the contrary, according to Weber's observations, nitric acid of 2 per cent. is not at all changed when cold by sulphur dioxide; there is no appreciable action below $80^\circ C.$, a temperature which, in normal work, is never approached in the lead chambers.

The researches of R. Weber in 1866 and 1867 (Poggendorff's 'Annalen,' cxxvii. p. 543, and cxxx. p. 329) have proved the complete futility, in all points, of Peligot's theory, and have greatly contributed towards elucidating the process within the lead chamber. Briefly, he states as follows* :—In the chambers, to 100 parts of sulphur, 220 parts of water are used, and from 6 to 8 parts, at most, of nitrate of soda. According to Peligot's equations the liquid at the bottom of the chamber could thus only contain from 2 to 2·3 per cent. of N_2O_5 , even without taking into account that, according to him, one third of the nitrogen passes as NO into the atmosphere of the chamber: $3 N_2O_4 = 2 N_2O_5 + 2 NO$. [Properly speaking, therefore, only 1·6 to 1·8 per cent. of N_2O_5 could be present in the chamber-acid.] Weber found,

* Some parts of Weber's as well as of Winkler's work have been noticed in Chap. III. p. 149 *et seq.*

by direct experiments, when sulphur dioxide was conducted into nitric acid containing even a higher percentage (viz. 3 per cent.) of N_2O_5 , that, at the ordinary temperature, after the lapse of half an hour no sulphuric acid at all had been formed, and extremely little at $40^\circ C$. (about the temperature of the chambers); whilst in the well-known laboratory experiment in a glass flask, from a mixture of SO_2 , NO , atmospheric air, and water there is an easy and instantaneous formation of sulphuric acid; and the lead chambers also produce this acid so quickly that the extremely slow action of nitric acid cannot account for it at all. Furthermore, Weber proved that Peligot was mistaken in supposing that nitrogen peroxide with water merely decomposes to NO and NO_2H , and that N_2O_5 cannot exist in presence of an excess of water; for water which has absorbed vapours of nitrogen peroxide liberates free iodine from a solution of potassium iodide, even when it has been heated to incipient ebullition; it must therefore contain N_2O_5 ; for neither pure nitric acid nor nitric oxide attacks potassium iodide.

Further, whilst dilute nitric acid has next to no action on sulphur dioxide at the ordinary temperature, there is a strong action between SO_2 and water which has absorbed the vapour of nitrogen peroxide, or if such water is added to the same dilute nitric acid which at first showed no action, or, more simply, if, instead of pure nitric acid, fuming nitric acid strongly diluted with water be used. *Accordingly, the nitrous acid generated by the contact of nitrogen peroxide and water oxidizes the sulphurous acid much more readily than nitric acid does; nitrous acid is therefore undoubtedly the primary cause of the reaction for the formation of sulphuric acid when moist air meets sulphurous acid and the vapour of nitrogen peroxide.* The nitric acid which is formed at the decomposition of N_2O_4 by water remains undecomposed by SO_2 *if much water is present.* Under certain circumstances, however, as will be shown below, the nitric acid is decomposed as well.

For the chamber-process the behaviour of N_2O_4 and N_2O_5 towards sulphuric acid of various degrees of dilution with water must also be taken into account, as those gases come into contact with such acids, both in the shape of minute drops suspended in the atmosphere of the chamber and in the shape of the stock collected at the bottom. According to their degree of dilution, the sulphuric acids contain nitrososulphuric acid (chamber-crystals),

free N_2O_4 , or N_2O_3 , as has been explained in detail on p. 151 *et seq.* but all these liquids, when their density is much higher than that of ordinary chamber-acid, are rapidly decomposed by sulphurous acid, sulphuric acid being formed. The decomposition of the absorbed vapours by means of water, for the purpose of forming nitric acid, is therefore quite unnecessary and improbable; but the water must serve for forming the hydrate SO_4H_2 , and therefore only in its presence can SO_2 be promptly oxidized by N_2O_3 .

It is of importance in practice that the more dilute mixtures containing nitric acid are more easily decomposed by sulphurous acid than concentrated ones. When nitrous acid is dissolved in the pure hydrate SO_4H_2 , or even in ordinary vitriol of 170° Tw., the sulphurous acid does not act upon it at all, or at least very incompletely.

When nitric acid is mixed with *dilute* sulphuric acid of varying concentration, it is seen that in a mixture of pure nitric acid of 1.25 spec. gr. with sulphuric acid of 70° Tw. the nitric acid is not decomposed by sulphurous acid in the cold, but quickly on being heated, with evolution of nitric oxide; in the case of stronger acids (from 77° Tw. upwards) the decomposition begins in the cold, and the liquid then contains nitrous acid. Evidently the sulphurous acid first produces nitrous acid in those mixtures, which is proved by their colour and by their action on potassium iodide; and in the *second* stage the nitrous acid yields up oxygen direct to the sulphurous acid, without being compelled, as Peligot assumed, to be redecomposed into nitric acid and nitric oxide—a preposterous assumption. Thus even dilute nitric acid, brought into contact with moderately strong sulphuric acid, may be useful for the chamber-process, as in that case the water is taken away from it, and in the concentrated state it is readily attacked by sulphurous acid; this is just what takes place in the chamber. Weber points out that Berzelius ('Jahresbericht,' xxv. p. 65) refuted Peligot's opinion that, in the chambers, no nitrous acid is formed from nitric oxide and atmospheric air, but merely nitrogen peroxide; eudiometric experiments with nitric oxide and oxygen have shown that, according to the excess of one gas or the other, there is more or less condensation, and that in any case there is always a formation of nitrous acid, even with an excess of oxygen (comp. p. 614).

According to the above argumentation, the water cannot play

the part which Peligot's theory attributes to it as the essential one, viz. that of decomposing N_2O_4 and N_2O_3 , and causing the formation of nitric acid. The water no doubt acts essentially by making possible the formation of sulphuric acid proper (SO_4H_2). With the modern opinions on the essence of acids this is a matter of course; and it is therefore unnecessary to cite the many experiments and arguments adduced by Weber as proof that the water disposes the sulphurous acid to oxidation. It should, however, be added at once that a quantity of water just corresponding to the formula SO_4H_2 , is not sufficient, because this strong acid would dissolve the nitrous gas, so as to form nitrososulphuric acid, and would thus withdraw it from the chamber-process; sufficient water must be used to decompose the nitrososulphuric acid and to form an acid of no more than 124° or 128° Tw.; then only does the chamber-process go on regularly, as we shall see below.

According to Weber's theory, the following process, therefore, goes on within the chambers. The sulphurous acid is oxidized, mainly by the oxygen of the nitrous acid, which thereby passes into nitric oxide; it does this, however, only when dissolved in water or in dilute sulphuric acid; and such a watery solution is formed either direct from free N_2O_3 , or by the decomposition of N_2O_4 . In the latter case, at the same time, nitric acid is formed, which can only be decomposed by the mediation of already formed sulphuric acid. The part played by the water has just been explained.

There is an agreement in many, but not in all points between the opinions of Weber and those published almost contemporaneously by A. Winkler (Untersuchungen &c. p. 20). Winkler also affirms the oxidation of sulphurous acid by nitrous acid; but according to him the part played by nitrogen peroxide is more essential than that which Weber assigns to it. Winkler believes the latter to be formed principally by the action of air on nitric oxide; it then combines with sulphurous acid and water to form nitrososulphuric acid, which sinks down to the bottom in the shape of the well-known mist, here comes into contact with the dilute hot chamber-acid and dissolves in it, evolving gaseous N_2O_3 , which oxidizes a new quantity of sulphurous acid, thereby passing into NO, the latter beginning the process anew.

The fact that Weber points more to N_2O_3 , Winkler more to N_2O as the active agents in the chamber-process does not form a

very essential difference in their views, as neither of them assumes either one of these oxides to be formed exclusive of the other. A more fundamental difference is this, that Weber, like Berzelius, does not admit the intermediate formation of nitrososulphuric acid as an essential feature of the process, whilst Winkler does so, thus coming back to Davy's theory, which he merely develops in the light of modern knowledge and more especially of his own investigations. Winkler's views are almost entirely compatible with the most modern theories on the subject, and have had to be modified only by eliminating N_2O_4 in favour of N_2O_3 , and by assigning to the formation and re-oxidation of NO the part of secondary reactions, as we shall see below.

It has been objected to the theories hitherto stated that there is a difficulty in assuming a simultaneous oxidation of nitric oxide and reduction of higher oxides to NO. But this objection cannot be held as valid, and it would apply to any other theory ever brought forward for the chamber-process, or, for that matter, for any other process where an "intermedium" or "carrier" comes into play. Although both processes undoubtedly take place at the same time, this may happen in the same chamber under different conditions: when in a certain part nitrous gas is reduced to nitric oxide, sulphurous acid vanishes at that part, and the excess of oxygen present everywhere can now oxidize the nitric oxide again: by currents, diffusion, &c. fresh sulphurous acid is brought in, and the process commences again. Besides, in any case the law of the action of masses comes into play, which may even cause qualitatively inverse reactions between the same substances, when their relative *quantities* are changed—for instance, the reduction of ferric oxide and formation of water in an atmosphere of hydrogen, and the oxidation of iron in an atmosphere of aqueous vapour. In a similar way the conditions in different parts of the chamber always differ so that both reactions take place at the same time.

When, in 1878, the first edition of this work was written, the question had not practically advanced beyond the labours of Weber and Winkler, both of whom relied on laboratory experiments, not on researches made with actually working vitriol-chambers. It was not even known what was the composition of the gases in normally or irregularly working chambers. The colour of the gases precluded the assumption that NO was the prevailing oxide of nitrogen, except perhaps in the first part of the system; it was

also known that nitric acid did not make its appearance except under very irregular circumstances. But the choice still lay between N_2O_3 and N_2O_4 as the prevailing constituent of the "nitrous vapours" in the vitriol-chamber, and it was not known which of these might be the real oxygen carrier. I myself at that time thought I had good reasons for assuming that in a *normally* working chamber, where there is neither too much nor too little oxygen, the nitrous acid greatly predominates over the nitrogen peroxide. This I inferred, 1st, because according to Winkler's and my own experiments nitric oxide in the presence of sulphuric acid of moderate strength, which is everywhere present in the chamber in the shape of a mist, is not oxidized beyond N_2O_3 even by an excess of oxygen; 2nd, because the nitrous vitriols analyzed by me never showed more than traces of higher oxides than N_2O_3 (that is, nitrososulphuric acid proper), whilst, for instance, when the pure nitrogen peroxide given off by heating lead nitrate was absorbed by sulphuric acid, a mixture of one molecule of N_2O_3 and two of HNO_3 was always formed. The different results found by several chemists (Kolb, Winkler, Hurter) with respect to their nitrous vitriols I referred to faulty analytical methods or else to irregular work. Where the formation of sulphuric acid ceases almost entirely in the last chamber, the condition for forming nothing but N_2O_3 is absent; and in that case first N_2O_4 , and then, by its contact with water, also HNO_3 will be formed. If, however, the free oxygen should be too much diminished, the sulphurous acid, then in excess, will at once reduce N_2O_3 and N_2O_4 to NO , and the chamber will turn pale. The same will happen when too much air enters, because then the gas gets too much diluted. When there is a deficiency of sulphurous acid (which in normal work ought not to happen), much of the nitrogen oxides will be converted by the oxygen in excess to N_2O_4 , which will be split up with the water into $N_2O_3 + NO_2.OH$. This, however, can only happen when the chamber-acid is very dilute; otherwise from the first only N_2O_3 is formed (see above), and therefore no $NO_2.OH$ will appear. (This is a succinct summary of my opinions, as held at the time when the first edition of this work appeared, on the strength of Weber's and Winkler's experimental researches.)

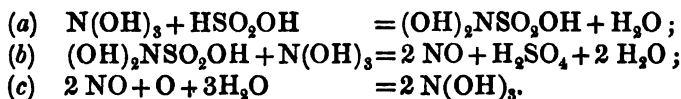
A solid basis for a true theory for the vitriol-chamber process could be created only by investigating the manufacturing process

itself in all its stages, and, both in the case of normal and of irregular work, by an extended series of gas-analyses and other pertinent observations. The first and hitherto the only complete investigation of this kind has been that made subsequently by myself in conjunction with Naef at the Uetikon works near Zürich, to which allusion has been made before (Chem. Ind. 1884, pp. 5-19). The results of this investigation have not been shaken by any others carried out since, so far as the facts of the case are concerned; but the explanations at that time given by myself and by other chemists have had to be modified considerably, especially in consequence of the further experimental work conducted by me in 1885 (J. Chem. Soc. xlvii. p. 465; Ber. d. deutsch. chem. Ges. xviii. p. 1384; comp. other work done before and after, mentioned Chap. III. p. 145 *et seq.*). I proved that in the *dry* state, and out of the reach of sulphuric acid, nitric oxide with an excess of oxygen combines to form nitrogen *peroxide* exclusively, or nearly so. If dry nitric oxide, being in excess, meets with an insufficient quantity of oxygen, a considerable quantity of N_2O_3 is formed along with N_2O_4 , and this N_2O_3 must necessarily have been in the state of *vapour*. In the presence of moisture, nitric oxide and excess of oxygen combine to form nothing but nitric acid. *Dilute* sulphuric acid (spec. grav. 1.405) acts on the whole like water, but a small quantity of nitrous acid is formed, as much as can exist in a stable solution in the acid (nitrososulphuric acid cannot exist in such dilute acid). Perhaps the most important observation, combined with others formerly made, was this:—If *strong* sulphuric acid is in presence of a large excess of oxygen, and nitric oxide is slowly passed into it, only that portion of NO which is in *immediate* contact with sulphuric acid, and so far as nitrososulphuric acid can be formed, is not oxidized beyond the state of N_2O_3 (as previously found by Winkler and myself); but all the gaseous molecules coming into contact with oxygen *outside* the acid, even immediately above it, behave like dry NO and excess of O generally, that is, they combine to form N_2O_4 .

This last observation made it impossible to maintain, as had been done in the first edition of this work, and in some of my later papers, that the reason why NO and O within the vitriol-chambers do not combine to form N_2O_4 , but merely N_2O_3 , is found in the fact that there is a mist of sulphuric acid floating all over; for the liquid particles of sulphuric acid forming that mist are

still at very great distances from one another relatively to the amount of molecules of NO and O present, and wherever the latter act upon one another otherwise than in immediate absolute contact with the acid, they will not yield N_2O_3 , but N_2O_4 . Hence no theory can be a true explanation of the vitriol-chamber process which presupposes the reduction of nitrous compounds to NO as a necessary step, for this would necessarily lead to the formation of N_2O_4 , and further on of HNO_3 , neither of which occurs in a regularly working vitriol-chamber. It is true that Raschig (Ann. d. Chem. ccxlviii. p. 135) asserts that nitric oxide, even when meeting a very large excess of oxygen, is not converted into N_2O_4 , but into N_2O_3 , provided that the oxygen is diluted with nitrogen, as in atmospheric air. But this assertion, which is opposed to the statements of all other chemists, has been entirely disproved by my researches (Berl. Ber. 1888, p. 3234), which showed that Raschig's experiments were badly conducted, and that by properly experimenting NO and air form principally N_2O_4 .

Raschig's own theory of the vitriol-chamber process (Ann. Chem. ccxli. p. 242) is very curious. He assumes as an intermediary link the temporary formation of a compound which he (somewhat inappropriately) calls "dihydroxylamine-sulphuric acid," of the formula $(OH)_2NSO_2OH$, but which nobody has seen, and whose preparation in the free state he himself does not hold to be likely to be effected. He assumes this compound to be formed when nitrous and sulphurous acid meet, but to be instantly decomposed with more nitrous acid into NO, SO_4H_2 , and H_2O ; NO is then again oxidized to nitrous acid, and the process begins anew. His equations are:



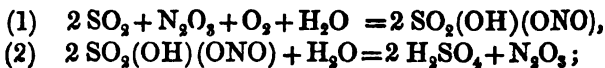
I have shown (Ber. d. deutsch. chem. Ges. 1888, pp. 67 & 3223) how utterly unfounded are all the arguments adduced by Raschig for his view, evidently in ignorance of the actual working of vitriol-chambers and in neglect of the laboratory work of former chemists; and we cannot waste our space here with repeating the refutation of a completely exploded theory*.

* This is all the less necessary as Hamburger (J. Soc. Chem. Ind. 1889, p. 104) has given a summary of the controversy for English readers.

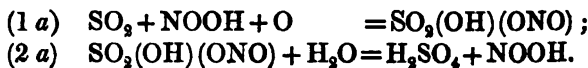
Several facts have to be reconciled in any true theory of the lead-chamber process: 1st, the fact that the chambers contain at first a mixture of NO and N_2O_3 , afterwards merely N_2O_3 , but never (in regular work) any N_2O_4 (Lunge and Naef's observations at Uetikon); 2nd, that NO and an excess of O combine to form N_2O_4 , and only where NO and O meet at the same time sulphuric acid of sufficient concentration they form nitrous acid, but not in the free state, merely in the shape of $SO_2(OH)(ONO)$; NO and O, in the presence of H_2O and SO_2 , may also form directly $SO_2(OH)(ONO)$. A new theory of the chamber-process, based on these fundamental and all other observed facts, had been clearly, although very briefly, indicated by myself in my before-mentioned paper of 1885 (J. C. S. xlvii. p. 470), and it has been further developed in subsequent papers, especially Ber. d. deutsch. chem. Ges. 1888, pp. 67 & 3323).

The fundamental ideas of that theory were expressed by me in 1885 as follows: "*Sulphur dioxide combines directly with nitrogen trioxide, oxygen, and a little water to form nitrososulphuric acid, which floats in the chamber as a mist; on meeting an excess of water, equally floating about as a mist [probably mostly or all in the shape of very dilute sulphuric acid], the nitrososulphuric acid splits up into sulphuric acid, which sinks to the bottom, and nitrogen trioxide, which begins to act anew. Hence it is not, as hitherto generally assumed, the nitric oxide, NO, but the nitrogen trioxide, N_2O_3 , which acts as carrier of oxygen in the vitriol-chamber process.*" As expressed later on, the formation of sulphuric acid is not brought about by alternate oxidation of NO to N_2O_3 or N_2O_4 , and subsequent reduction of these compounds to NO, but by a condensation of nitrous acid with sulphur dioxide and oxygen into nitrososulphuric acid, and a subsequent splitting up of this compound by an excess of water.

The reactions here indicated are expressed by the equations:



but they assume even a simpler shape, if, in lieu of nitrous anhydride, nitrous acid is introduced into the equations, thus:

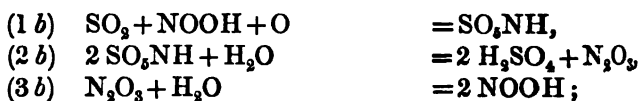


At the same time I pointed out that these reactions were or might be locally modified by special circumstances in different parts of the chamber, and this matter was treated in detail in my papers of 1888.

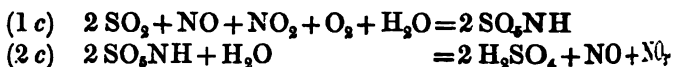
We see at once that my theory goes back to Davy's theory of 1814, subsequently upheld, among others, by L. Gmelin and Cl. Winkler, according to which the intermediate formation of nitroso-sulphuric acid (chamber-crystals) is a necessary link in the chamber-process. But my new theory removes the complication of those former views, and their partial contradictions to observed facts, by denying the necessity of a reduction to NO as an indispensable factor in the process, from which reduction would follow the formation of N_2O_4 in the chamber. We will now follow up the new theory in detail and consider the modifications which the process suffers by local circumstances in certain parts of the chamber.

Let us remember that the gases of a normally working chamber contain at first a mixture of NO and N_2O_3 , further on and right to the end only N_2O_3 . Nitrogen peroxide, N_2O_4 , can be found only in case of irregular work, when by sending an unnecessary excess of nitrous gases into the chambers the formation of sulphuric acid has been finished too early, and the last part of the chambers contains extremely little SO_2 ; in this case there, but only there, N_2O_4 is found. A greater or smaller excess of oxygen is without any influence on the question whether N_2O_3 or N_2O_4 is formed. The assumption that the N_2O_3 found by Lunge and Naef was only a mechanical and accidental mixture of NO and NO_2 (or N_2O_4) is altogether at variance with the facts, as shown in the original, and this is even independent of the question strongly disputed among a number of chemists (Witt, Lunge, Ramsay and Cundall, &c.), whether nitrous anhydride can be proved to exist in the state of vapour, or whether, on the contrary, N_2O_3 dissociates *completely* after evaporation, or after being set free from the salts of nitrous acid, into nitric oxide and nitric peroxide (a *partial* dissociation is not denied by anybody). Even in the latter case N_2O_3 would certainly exist for a moment after being set free from SO_2NH by the action of water; and this might suffice for again combining it with SO_2 , O_2 , and H_2O , or else we must assume that its components $NO + NO_2$ act in the same way, the NO not finding time to oxidize into NO_2 , as SO_2 intervenes at once, and

thus SO_5NH is formed. According to the former (my own) view the orange vapours filling the chambers consist of N_2O_3 , which is constantly being absorbed by H_2O , SO_2 , and O , and re-formed from SO_5NH and H_2O ; according to the latter view they would be a mixture of NO and NO_2 , existing but for a moment in order to be absorbed for the formation of NOOH , or directly of SO_5NH , and to be constantly re-formed from the latter compound as before. That the second view is much less likely to be true than the first is shown in the 'Berichte,' xxi. p. 74; but either view is compatible with my theory, which in the second case would have to be formulated thus:

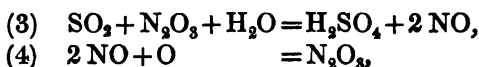


or else:



In accordance with the practice followed in the preceding portions of this book, we shall not hamper our considerations by entering upon the complicated formulæ involved in the last-mentioned way of looking at nitrous anhydride, but we shall treat this compound as capable of existing in the state of vapour at least for a sufficient time to enter into the reactions (1); but those who prefer to do so may in lieu of this make use of reactions (1 a) or (1 c).

The reactions formerly assumed by Berzelius (with the qualification expressed on p. 606), R. Weber, myself, and, although but indirectly, by Raschig, namely:



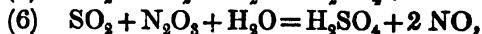
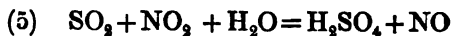
cannot represent the chamber-process; for, firstly, in this case there would be everywhere in the chambers, up to the end, a large number of molecules of NO together with N_2O_3 , which is not the case, and, secondly, the reaction (4) does not take place at all, at least to an appreciable extent, seeing that there is an excess of oxygen all over the chamber, except in *immediate* contact with (strong) sulphuric acid; but in contact with sulphuric acid there is no free N_2O_3 formed, but SO_5NH , and we are thus forcibly brought

back to reactions (1) or to reaction (7), mentioned later on. If in the back parts of the chambers NO existed to any extent in the free state for any appreciable length of time, it must there be oxidized into nitrogen peroxide, and this in contact with either water or sulphuric acid must form nitric acid, which must be found at least to a great extent unchanged, as it is a sufficiently stable compound in that part of the chamber, where there is far too little SO_2 and too low a temperature to reduce much HNO_3 . But since HNO_3 is *not* found in normal working back-chambers, nor in the Gay-Lussac acid, *any theory based on the reduction of nitrous vapours down to nitric oxide, NO, cannot be accepted as true*, as it involves the formation of N_2O_4 and subsequently that of HNO_3 .

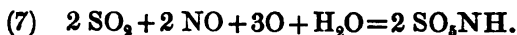
It is important for our theory to notice that sulphuric acid, such as found in the chambers, certainly dissolves very sensible quantities of SO_2NH , and indeed all the "drips" and even the bottom acid of the back-chambers testify to this. But this solubility, or, as it is better expressed, the stability of SO_2NH is greatly diminished both by a higher temperature and by dilution of the acid (comp. Sorel's tables, p. 158, and my new tables, to be given in the Appendix), and this behaviour is indeed the foundation of all former processes for denitrating nitrous vitriol (p. 560 *et seq.*). In the vitriol-chambers the temperature is much above that of ordinary air; the second condition is also fulfilled, for as soon as the SO_2NH formed in one place, and floating about in the shape of a fine mist, meets with particles of water or of dilute sulphuric acid, floating about as well, it must suffer decomposition according to equation (2), so that sulphuric acid and nitrous acid are formed. Only those portions of nitrososulphuric acid which are in immediate contact with the bottom acid will be dissolved by this, and will thus be temporarily withdrawn from decomposition; but this takes place to a somewhat greater extent only in the back chambers, whilst in the front chamber, where both the higher temperature and the excess of SO_2 act as denitrating agents, the bottom acid shows little or sometimes even no "nitre."

The views hitherto brought forward do not, however, explain the whole of the vitriol-chamber process; they must be modified for the first part of the chambers, which is filled with opaque white clouds, and where Lunge and Naef have proved the existence of much NO together with N_2O_3 . The temperature is highest and

the formation of acid most vivid in this region. It is not itself impossible that here the direct reactions take place :



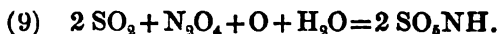
which would explain the occurrence of NO. The latter, when meeting SO_2 and O, both present here in large excess, form directly nitrososulphuric acid :



Locally, where water is in excess, nitric acid will be formed, but here, where this acid is in the state of vapour, and where it at once meets an excess of SO_2 , it is at once reduced by the reaction :

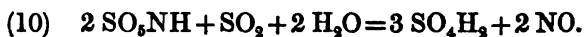


In fact in this first part of the chambers the conditions are still altogether analogous to those prevailing in the immediately preceding Glover tower, and are entirely different from those prevailing in the back part of the chambers, where the temperature is lower and there is very much less SO_2 present. In the front part the NO finds such an excess of SO_2 , O, and H_2O , that the formation of N_2O_4 is either altogether precluded, or if any small quantity of it is formed it must be instantly absorbed again, according to equation :



In the first part of the chamber system nitrogen peroxide does not and cannot exist in appreciable quantities, and therefore the formation of sulphuric acid according to equation (5) does not play any, or no appreciable, part. Equation (6) is practically on the same lines.

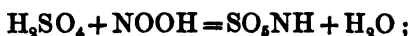
This does not yet explain why there is in fact a large quantity of NO present in the first part of the chambers. We seek this explanation in a secondary reaction which under the existing conditions is bound to occur, viz. :



This is, of course, precisely similar to that which takes place in the immediately preceding space, that is, in the Glover tower, the conditions being identical in both cases : presence of large quantities of nitrososulphuric acid, of SO_2 , of H_2O , and an even higher temperature than near the top of the Glover tower, where the inflowing acid has a cooling action. Thus more NO is formed than can be at once taken up by reaction (7).

The general results arrived at are as follows:—The *principal reactions* conducive to the formation of sulphuric acid in the vitriol-chambers are, the *formation of nitrososulphuric acid* from sulphur dioxide, oxygen, and nitrous acid (eq. 1), and its subsequent *decomposition* when meeting with water or dilute sulphuric acid (eq. 2). Whether we assume N_2O_3 to exist for an appreciable time as undecomposed vapour or not, is not a decisive point in this case, as we may introduce the hydrate $NOOH$, or may assume that the components $NO + NO_2$ act just as N_2O_3 . Besides this principal reaction, another set of reactions take place in the first part of the chambers, where the nitrososulphuric acid is partially denitrated by the excess of sulphur dioxide (eq. 10), and the nitric oxide thus formed combines directly with SO_2 , O , and H_2O to re-form SO_2NH (eq. 7). All the other reactions enumerated above play either no part whatever, or only an insignificant part in the chamber-process, and nitrogen peroxide especially does not occur at all in normally working chambers.

The mutual action of the agents meeting in the vitriol-chambers evidently belongs to the class of *reversible reactions*, whose direction in one sense or another is determined by certain special conditions, usually by the "action of mass," one or several of the components being in excess. If oxygen or nitrous acid is in excess, the condensing reactions (1) and (7) prevail, and thus the formation of nitrososulphuric acid is induced; but if sulphurous acid is present even only in *relative* excess, the denitrating reaction (10) prevails, and NO is split off. This does no harm in the first part of the chambers, where there is time for the NO to enter into the condensing reaction (7), but if it happens in the back part, the NO is lost, as it is not retained in the Gay-Lussac tower and escapes into the air. Another reversible reaction is that between sulphuric acid, nitrous acid, and water; where the sulphuric acid is in excess, we have:



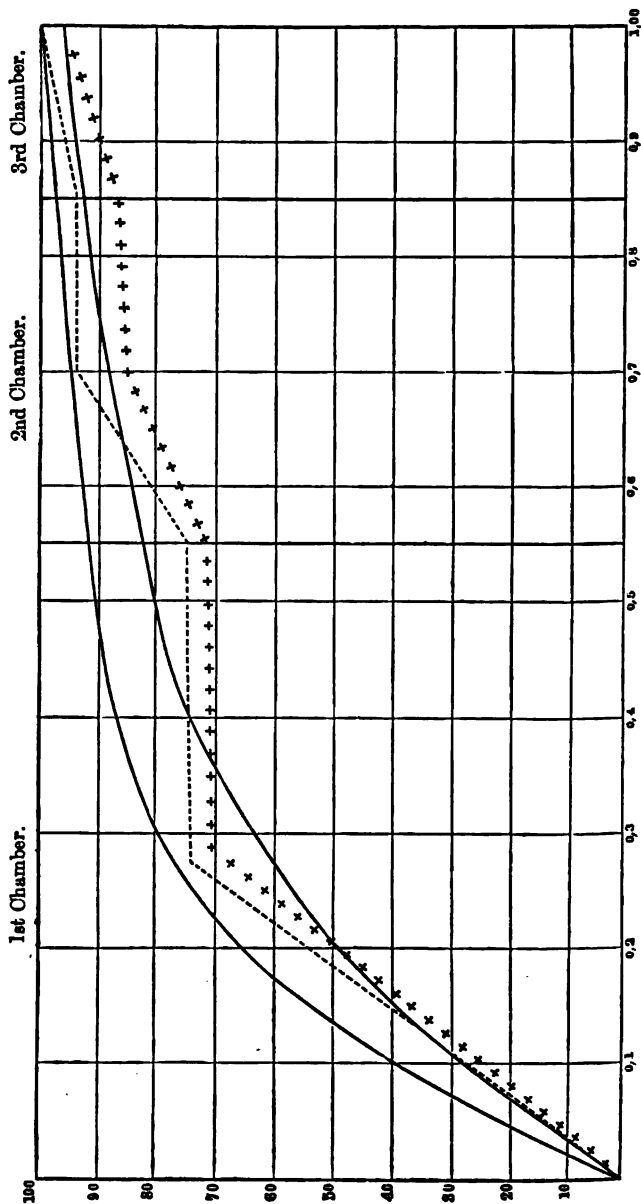
where, on the other hand, water is in excess, we have:



Nothing is more certain in the manufacture of sulphuric acid than that the process of converting sulphurous into sulphuric acid takes place in a regular way only by the action of a large excess of

oxygen and of nitrous vapours ; with a smaller excess of the

Fig. 289.



agents sulphur dioxide escapes into the air. Even with the greatest excess of oxygen it is not possible to effect an absolutely complete oxidation of SO_2 ; it is generally agreed that the best practical limit is attained if the exit gases contain 0.5 per cent. of the sulphur originally employed in the shape of SO_2 . The rate at which the formation of sulphuric acid takes place under the given conditions of a certain excess of oxygen and of nitrous vapours has been mentioned before (p. 483), as observed experimentally. It has also been mathematically deduced, first by Hurter (*J. Soc. Chem. Ind.* 1882, p. 52), afterwards by Sorel (in the frequently quoted paper), but their calculations lay claim to interest mostly on the ground that they are in general accordance with previously observed facts, and, being founded on the differential and integral calculus, they would be unintelligible to the great majority of the readers of this treatise; we must therefore refer those interested in them to the originals. Both authors also represent the normal working of the chambers by curves, with which Hurter compares the practical results of Mactear, and Sorel those of Lunge and Naef (which were not published at the time of Hurter's theoretical research). We have previously (p. 490) compared Hurter's curves with the latter; in this place we will give the diagram in which Sorel represents the process (fig. 239), both by his theoretical curves (drawn in full lines)—the upper one representing a loss of 0.5, the lower one a loss of 4 per cent. of sulphur—and the results obtained by Lunge and Naef (in dotted lines). I have already (p. 491) pointed out that whilst on the whole the rate of formation of the acid is in agreement with the theoretical curves, there are distinct breaks corresponding to the points where the gases leave one chamber to enter into the next, and we have to some extent gone into the explanation of this phenomenon. But it is now the time to give Sorel's explanation, which, although in full agreement with my theory of the vitriol-chamber process, simplifies it by specifying more distinctly the conditions under which either the first or the second of the main reactions,



takes place.

In an inert atmosphere nitrous sulphuric acid will give up more or less N_2O_3 , according to the concentration of the sulphuric acid, the quantity of nitrous (or nitrososulphuric) acid, and the tem-

perature. If a certain quantity of N_2O_3 is removed from the surrounding gases, either directly or by reduction to NO, the acid will yield up more N_2O_3 ; if, on the other hand, the surrounding atmosphere becomes richer in N_2O_3 by oxidation of NO, the acid will take up some N_2O_3 again. The tension of N_2O_3 in its solution in H_2SO_4 is increased by a rise of temperature, but much more by diluting the acid. If, therefore, there exist in an atmosphere, containing a certain quantity of N_2O_3 , two solutions of N_2O_3 in sulphuric acid, one of them in concentrated, the other in dilute sulphuric acid, the former will enrich itself in N_2O_3 at the expense of the latter, even if it be to a certain extent hotter than the latter. Even the presence of SO_2 does not prevent the solution of N_2O_3 in sufficiently concentrated acid, provided that oxygen is present in excess and that the tension of the N_2O_3 (actually present or possible to be formed from NO and O) is greater than that of the acid in question. On the other hand the SO_2 will decompose (*i. e.* denitrate) the acid if the outer tension of N_2O_3 is less than that of the acid, or on diluting the latter, or on raising the temperature. [These are indisputable facts, well known before Sorel, but very clearly put by him with the addition of bringing in the "tension" of N_2O_3 , about which he could not have known very much in detail; much more material for deciding these questions has been furnished by my own and my assistant's investigations, to be mentioned in the "Appendix."]

We will, for instance, assume a certain definite quantity of acid of 57° B. ($=130.4^\circ$ Tw.), containing so much N_2O_3 that for a certain temperature the equilibrium with the surrounding gaseous mixture is established. This acid hovers as a mist in the gaseous mass. Suppose a certain volume of this gaseous mass is cooled down, the pressure remaining the same; then part of the aqueous vapour contained in the gaseous mixture will be precipitated in liquid form and will dilute the acid. The acid will thus become incapable of withdrawing all its N_2O_3 from the influence of the SO_2 present; some NO will be formed, but also some H_2SO_4 , by which the acid becomes more concentrated. If now the gaseous mass is brought back to the former, higher, temperature, the acid must, corresponding to the rise of temperature, yield up aqueous vapour, till it has again attained the density $=57^\circ$ B., at which it once more fixes NO and O in the shape of N_2O_3 .

Leaving out of consideration the secondary reactions, Sorel

like myself, looks at the intermediate formation of nitroso-sulphuric acid (the fixation of oxygen upon sulphur dioxide by means of nitrous acid) as one of the principal reactions, followed by the decomposition of that compound, by dilution with water, into sulphuric acid and nitrous acid.

The principal cause for determining the reaction in this or that sense is a change of temperature. We have seen before (pp. 476, 480) that the temperature near the leaden walls of the chamber is considerably less than that of the inner parts; therefore the gases must assume a quick rotation round a nearly horizontal axis, and each minute drop of acid, according to the change of vapour-tensions, must first be concentrated in the central portion and then be diluted again near the walls. Suppose we have a chamber-acid of 116° Tw. or 67 per cent. H_2SO_4 . If, as was the case in a special experiment, the temperature next to the walls is $=75^{\circ}$, that in centre $=90^{\circ}$, the vapour-tension of 67 per cent. acid next to the wall will be $=27$ millim. (comp. the table p. 137); and since the acid hovering in the centre must have the same vapour-tension, but the higher temperature of 90° , its concentration (according to the same table) must be $=73$ per cent. H_2SO_4 or $=130^{\circ}\cdot4$ Tw. If, for instance, the acid near the wall had contained only 64 per cent. H_2SO_4 , its vapour-tension would have been $=37\cdot4$ millim., and the hotter acid in the centre would at equal tension have contained 71 per cent. $=126^{\circ}$ Tw. A number of observations made by Sorel at working-chambers prove that the above-supposed differences do exist, which proves that the assumption of an equal vapour-tension all over the chamber is a correct one, and consequently also the assumption that regularly the concentration of the acid is greater near the centre than near the walls, where the cooling action of the air is at play. But as the greater concentration of the acid favours the fixation of nitrous vapours by SO_2 and O, in the shape of SO_2NH , and the greater dilution the decomposition of this compound into H_2SO_4 and N_2O_3 , it follows that the formation of SO_2NH takes place principally in the centre, and that of real H_2SO_4 principally near the walls. The neighbourhood of the walls thus increases the production, as the cooling brings about the condensation of water, the dilution of the nitrous acid, and its decomposition into H_2SO_4 and N_2O_3 . To a smaller extent this is also effected by the neighbourhood of the acid layer

at the bottom, which is both cooler and more dilute than the acid floating about in the centre. All this is indirectly, but certainly, proved by the fact that a few centimetres from the wall, where the formation of H_2SO_4 must be strongest, and equally a little above the bottom acid, the greater intensity of the reactions is manifested by a rise of temperature.

As the gaseous current moves nearer the end of the chamber it becomes poorer in SO_2 , and the reactions are therefore less intense. Moreover, observation shows that the temperature in the second half of the chamber hardly sinks at all in the centre, and but 2° near the walls. Less H_2SO_4 being made in this part, the acid in the centre is more dilute, and less able to fix N_2O_3 and SO_2 in the shape of SO_4NH , and that at a time when the smaller quantity of SO_2 anyhow makes this reaction more difficult. This, according to Sorel, explains the almost total cessation of the reactions in the back part of the first chamber, observed by Lunge and Naef; and it also explains the revival of the process in the second chamber, observed by them, as the gases are *cooled* near the end walls of the chambers and in the connecting-pipe to the extent of 20° or 30° C. In fact a chamber exposed on the north side to the free air, and on the south side to the radiation from a second chamber, made at the north wall $2\frac{1}{2}$ times more acid 3° Tw. stronger than at the south wall.

There must be a close connection between the temperature at the chamber-wall, the nitrous-acid tension, the intensity of the reactions at any given point, and the outside temperature. For every description of chambers, every special place in them, and every rate of manufacture, a certain temperature must be the most favourable—that which causes neither too much nor too little vapour-tension under the given circumstances. Both when the temperature is too high and when it is too low more nitre is used than under normal conditions [the damage done by too low a temperature is doubtful; compare the Freiberg experiences, p. 473]. In the case of the forced style of working, where the temperature is higher to begin with, any rise of the outward temperature makes less difference. Latterly many [French] manufacturers have adopted this forced style (brought about by a very large supply of nitre, by means of ample Gay-Lussac and Glover space), where the draught is better and the cost of plant less; but this can only be done with medium-sized chambers, as otherwise the heat rises

too much at the commencement. Nor is it possible to diminish the chamber-space below 0·8 cubic metre per 1 kilog. of sulphur burnt in 24 hours (say 12·8 cubic feet per lb. of sulphur) without damaging both the chamber-lead and reducing the yield by the intense heat.

We see how important, in Sorel's view, is the part played by the division of the total chamber-space into several chambers. Although many of his reasonings are not strictly proved as yet, more especially those referring to the "tension" of nitrous acid in contact with sulphuric acid, even these bear the appearance of inherent probability; and altogether we cannot doubt that in reality the cooling-action of the chamber-walls and ends and of the connecting-pipes is very important. But Sorel does *not* explain why, according to his own showing, the chamber temperature sinks very little in the second half, and very little acid is made there, although the surface of lead on this part of the two long sides and the roof is very much larger than on the two ends and the connecting-pipes taken together.

This seems to prove that the cooling is nothing like the *all*-important factor assumed by Sorel, and that the more intimate mixture of gaseous and liquid particles in the connecting-pipes, long ago adduced by me, and the shock against the solid surfaces must be equally acknowledged as potent factors for explaining the anomaly exhibited in the curves, fig. 239, p. 622. In my own proposals for modifying the chamber system, as explained on p. 380, all the influences for reviving the chamber process are brought into action,—that of an intimate mixture, of the shock against solid surfaces, and of the dilution of the acid by water, which at the same time serves as a cooling agent.

Irregular Working (Loss of Nitre).

Having so far stated the conditions of the *normal* vitriol-chamber process, we must also consider how the process may become *anomalous*, that is *faulty*, which must, in every case, lead to losses, both of nitre and of sulphur compounds.

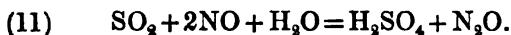
Sometimes *nitrogen peroxide* appears in the last chamber (never before). It has been proved by Lunge and Naef (Chem. Ind. 1884, p. 8) that this happens when the supply of nitre is abnormally strong, irrespective of a larger or smaller excess of oxygen,

of which there is always far more than enough present. In this case the formation of sulphuric acid is finished before the proper time; there is next to no SO_2 in the last chamber, and the nitrous anhydride, which cannot be again taken up by reaction (1), p. 616, is gradually dissociated into NO and N_2O_4 , the former being equally oxidized to N_2O_4 . The latter where it touches the chamber acid dissolves in it and forms both nitrous vitriol and nitric acid. Most of the N_2O_4 , however, with the remaining N_2O_3 , passes into the Gay-Lussac tower; and as the size of this apparatus is only calculated to meet normal requirements, it cannot retain all the nitrous vapours, but emits a good deal of it into the air in the shape of ruddy vapours, thus causing a corresponding loss of nitre.

Far more serious are the consequences of a *lack of nitre* (comp. Chapter VII. pp. 462 *et seq.*). In this case the formation of sulphuric acid is too slow, and there is too much SO_2 in the back part of the chambers, thus causing a denitration of SO_5NH in the *wrong* place, according to eq. 10 (p. 620). Very much NO is formed, the chambers turn pale yellow, or, in extreme cases, grey, and the temperature is either too high or too low for proper working. Owing to the relative excess of water the formation of the intermediate compound SO_5NH is greatly impaired; and the NO now forms with oxygen and water nitric acid, which sinks down to the bottom and dissolves unchanged in the chamber acid, and is thus withdrawn from the chamber-process. Such acid will not "show nitre" in the sense used by practical men—that is, it will not give out orange vapours on addition of water, because it contains little SO_5NH , but for all that it may contain so much nitric acid that the chamber-lead is seriously attacked. The nitric oxide, on passing into the Gay-Lussac tower, is not absorbed at all by the sulphuric acid, the excess of inert nitrogen preventing its action with SO_2 and O , and at the top both NO and SO_2 escape, thus causing a double loss. A third source of loss is the formation of nitrous oxide, N_2O , for which the conditions now exist to a much greater extent than normally (see below). All this leads to a bad yield of sulphuric acid from the first and to a great loss of nitre, and as this instantly reacts upon the chamber-process, the floating quantity of oxygen-carriers being diminished at a progressive rate, it is no matter of surprise that things get from bad to worse. Every practical man knows, and Eschellmann has proved it in

detail (J. Soc. Chem. Ind. 1884, p. 136), that when there has been lack of nitre from any cause whatever it is necessary to introduce *several times* the amount originally wanting or "saved," in order to remedy the "disease" of the chambers, as some people call it.

Another way in which nitre may be lost is by the formation of *nitrous oxide*, N_2O . We have seen in Chap. III. (p. 150) that this may happen if NO (or N_2O_3) meets an excess of SO_2 in the presence of water or of very dilute sulphuric acid. The reduction may then take place according to the equation—



It is not impossible that, under specially unfavourable circumstances, the reduction may even proceed as far as the formation of elementary nitrogen or of ammonia, but this evidently happens only quite exceptionally and to an altogether insignificant extent; whilst most chemists assume the formation of N_2O to occur to a small extent, even in normally working-chambers, at the places where locally water and sulphur dioxide are in excess. Actual proof of this, by showing the presence of N_2O in chamber-gases, has never been given; in fact, the analytical methods so far at our command would hardly permit this.

It is notorious that in no case whatever is the recovery of the nitrogen oxides, active in the manufacture of sulphuric acid, complete. Even with the best nitre-recovery and denitrating apparatus, and under the best possible management, the loss is never below 2 parts of $NaNO_3$ to 100 of sulphur burnt, and it is nearly always higher than that, 4 parts of $NaNO_3$ probably representing the ordinary present average. The sources of this *loss of nitre* are various, and may be distinguished as mechanical and chemical losses. *Mechanical losses* are those caused by incomplete absorption of N_2O_3 or N_2O_4 in the Gay-Lussac tower, by the nitrous acid contained in small quantities in nearly every description of sulphuric acid withdrawn from the process for sale or use, and by any accidental leakages from working-doors, chambers, &c. *Chemical losses* are those caused by the reduction of the nitrogen oxides below the point where they can be re-oxidized or absorbed in the Gay-Lussac tower. Generally this chemical loss is ascribed to a reduction to the state of nitrous oxide, or even elementary nitrogen, or (by Raschig) to that of ammonia; but the latter,

according to Raschig's own statement, is found only in quite exceptional circumstances and need not be taken into account for ordinary purposes. That a reduction to N_2O does take place under certain circumstances (excess of SO_2 and undue local excess of water) has been proved by R. Weber and by myself (p. 150); and it is likely that to a certain extent such conditions do obtain in every vitriol-chamber, but less than anywhere else just in the Glover tower, where such loss was at one time believed to take place (p. 571). It is, however, entirely uncertain what proportion the mechanical and chemical losses bear to one another. The most extraordinary discrepancies exist in this respect. Some chemists assert that the mechanical loss, more especially that caused by incomplete action of the Gay-Lussac tower, is by far the most potent source of loss of nitre (Lunge and Naef, Chem. Ind. 1884, p. 11; Benker; Sorel, Zeitschr. f. angew. Chem. 1889, p. 279); others are of the contrary opinion. It seems useless to go into the detail of this controversy here, as no conclusive proof has been given either way, and we will only quote some of the other papers bearing on this question: Hurter, Davis, Jackson, Mactear, Cox, and Lunge, in vol. xxxix. of the 'Chemical News' (pp. 170, 193, 205, 215, 227, 232, 237, 249); Eschellmann (J. Soc. Chem. Ind. 1884, p. 134); Hamburger (*ibid.* 1889, p. 167).

It is a fact that, by enlarging the Gay-Lussac towers beyond the size formerly used, the loss of nitre can be greatly reduced, and mention of this has been made before (p. 514). But it would seem as if the practical limit in that respect had been already reached when the Gay-Lussac towers, with ordinary coke-packing, have a capacity of 2, or at most of 3, per cent. of the chamber-space. Any further addition of absorbing-power causes but an insignificant diminution of the loss of nitre. The cause of this is no doubt that pointed out by Bailey (J. Soc. Chem. Ind. 1887, p. 92), that the coefficient of solubility of N_2O_3 in sulphuric acid is immensely reduced by its enormous dilution in the exit-gases with oxygen and nitrogen, and that therefore a complete absorption of N_2O_3 is an impossibility; and Sorel (in the place quoted above) proves a similar reasoning by observation and calculation, showing that, in a special instance, the exit-gases were bound to carry away nitrous acid equivalent to 3.09 per cent. of $NaNO_3$ to 100 of sulphur—that is, more than the best working factories consume altogether. It is true that direct analyses of the exit-gases in

most instances fail to account for more than a portion (say a third or even a quarter) of the nitre lost; but it cannot be denied that this may simply be an unavoidable fault of the analytical methods used, as it is extremely difficult, or rather impossible, to retain in absorption-tubes all the N_2O_3 or N_2O_4 diluted with ten thousand times its volume or more of other gases. Any reasoning based on the analysis of exit-gases is therefore extremely unsafe, if it intends to prove that the loss from that source is too small to dispense with the necessity of assuming a considerable chemical loss.

It is even more difficult to estimate NO than N_2O_3 when mixed with a very large excess of other gases, and hence the above-mentioned conclusions are all the more uncertain. The loss of NO may be reckoned partly among the mechanical and partly among the chemical losses. The former is the case when any NO which has come from the chambers themselves has only mechanically escaped oxidation into N_2O_4 and consequent absorption in the Gay-Lussac tower; but it must be reckoned as chemical loss if the NO has been formed within the Gay-Lussac tower itself by some reducing action on nitrous vitriol. We have seen that such an action may take place by an accidental excess of SO_2 (p. 558); but this happens only exceptionally, although it is possible that the SO_2 , always present in exit-gases even with the very best work, in spite of its very slight quantity exerts a certain reducing-action in the Gay-Lussac tower. Hjelt (Dingl. Journ. ccxxvi. p. 174; comp. also our 1st edition, p. 570) ascribed a certain loss of nitre to the oxidation of arsenious to arsenic acid in the Gay-Lussac tower, amounting to 0.12 nitre per 100 of H_2SO_4 made, and Davis (Chem. News, xxxvii. p. 155) went even much further in that respect; but the latter did not uphold his views later on, and even Hjelt's observation seems to have been quite exceptional, to judge from observations communicated to me in a letter from Dr. Th. Ernst, of Lehrte. Evidently arsenious acid can play but a very small part indeed in that matter.

A more important part in the loss of nitre is borne by the *coke-packing* of the Gay-Lussac towers. I had long ago (comp. pp. 160, 519) proved that the coke reduces any nitric acid getting into the Gay-Lussac acid in the shape of N_2O_4 , so that the nitrous vitriol issuing at the bottom contains only N_2O_3 . Recently I

have shown (in the same place) that nitrososulphuric acid itself is reduced by coke, NO escaping. This action is greatly increased by a higher temperature, and this may be one of the reasons why it is expedient to cool both the gases and the absorbing-acid as much as possible; it also seems to favour the use of Gay-Lussac towers containing a non-reducing packing (p. 549).

Calculations have been made as to *how long the gases remain in the lead-chambers* before the manufacture of sulphuric acid is complete. This matter is treated at length in our first edition, vol. i. p. 455 *et seq.*; here we will only mention that Schwarzenberg calculates that the gases pass through the chambers in $5\frac{3}{4}$ hours, Bode that they take $3\frac{1}{4}$ hours, and I myself (assuming a chamber-space of 20 cubic feet per lb. of sulphur and burner-gases with 8 per cent. SO_2) reckon $2\frac{3}{4}$ hours. It is also there calculated that, assuming a consumption of 4 parts of pure sodium nitrate to 100 parts of sulphur burnt, the nitre-gas does its oxygen-carrying work 130 times over before it is lost in some shape or another. Sorel calculates that in a system working on the "forced" plan, with only 0.7 cubic metre per kil., or 11.2 cubic feet per lb. of sulphur burnt (in winter), the gases take only 1 hour 34 minutes to pass through the chambers.

CHAPTER X.

THE PURIFICATION OF SULPHURIC ACID.

COMMERCIAL sulphuric acid, as it is produced in the chambers, always contains a number of impurities, partly owing to the raw material, especially the pyrites, employed, partly from the nitre, the water, the lead of the chambers, &c. Since this acid, if at all, has to be purified at the stage at which we have now arrived, viz. as chamber-acid, before being concentrated, we shall now treat of this matter, although, in the great majority of works, the chamber-acid is never purified, nor is there any occasion for it. For the sake of completeness, we shall here describe also the manufacture of pure distilled oil of vitriol, although this already presupposes the concentration of acid on a large scale, to be described hereafter.

The essential impurities of chamber-acid may consist of:—arsenic acid, arsenious acid, antimonie oxide, selenium, thallium, lead, iron, copper, lime, aluminium, alkalies; further, sulphurous acid, nitric acid, nitrous acid, nitric oxide (in the presence of ferrous sulphate), organic substances. According to Kuhlemann, for instance (Wagner's Jahresb. 1872, p. 253), the acid of two Harz works contained to each 100 grams SO_3 :—

	a.	b.
Arsenic.....	0·0088 grm.	0·0174 grm.
Antimony.....	0·0394 „	trace.
Copper	0·0013 „	„
Iron	0·0081 „	not estimated.
Zinc	0·0087 „	„
Lead.....	trace	0·0231 grm.

According to Bräuning (Preuss. Zeitschr. für Berg- &c. Wesen, 1877, p. 142), the chamber-acid at Oker in the Harz contains on the average 0·05 per cent. of arsenic and 0·008 per cent. of antimony. According to information I have received from the Freiberg

smelting-works, the chamber-acid there generally contains 0.02, but sometimes as much as 0.14 per cent. of arsenic.

Selenium occurs very frequently in sulphuric acid, where its presence is more and more noticed (*e.g.* Davis, J. Soc. Ch. Ind. 1883, p. 157, and Lunge, Ch. Ind. 1883, p. 128); its occurrence in the flue-dust and the chamber-deposit is well known.

Most of these substances occur partly in too small a quantity in the vitriol to be injurious, and they are partly without any influence for most uses of the sulphuric acid; the lead, for instance, is almost entirely precipitated on diluting the acid—the iron during its concentration in the platinum still, in the shape of pink crystals of anhydrous ferric sulphate. Lead, iron, (and arsenic) are said to be removable by electrolysis (J. of the Franklin Institute, v. p. 65). Lead is to be removed by hydrochloric acid (Teed, E. P. 17612, 1887). Special importance attaches, at least in some cases, to the removal of arsenic, especially when the pyrites contains very much of it, and to that of the nitrogen compounds—the latter when the acid has to be concentrated in platinum vessels.

The Purification of Sulphuric Acid from Arsenic.

Arsenic is found rarely, and never in more than traces, in acid which has been made from brimstone: most of the latter material, by far, is used where acid free from arsenic is wanted. On the other hand most kinds of pyrites contain arsenic; and the acid obtained from them is therefore arsenical—but in very different degrees, according to the percentage of arsenic in the pyrites and to the mode of manufacture.

The percentage of arsenic in pyrites is stated very differently: whilst most analyses of the ordinary ores only show "traces" up to fractions of 1 per cent., H. A. Smith asserts that he has found much larger quantities in the ores most commonly employed, viz. in Westphalian pyrites 1.878, in Belgian pyrites 0.943, in Spanish 1.651, in Portuguese 1.745, in Norwegian 1.649–1.708 per cent. of arsenious acid. These analyses are not quite to be relied upon, since their results differ so much from all others. Nor can we accept his estimations of arsenic in the various products of the alkali manufacture, derived from the original arsenic in the pyrites, his results being extraordinarily high (details in our first edition, p. 462).

Hjelt (Dingl. Journ. ccxxvi. p. 174) found in Westphalian pyrites only 0·30, in Norwegian only traces, in Spanish pyrites on an average 0·91 per cent. of As. Of the latter there remained in the impurities 0·19 per cent., in the saltcake none; in the hydrochloric acid: (a) pan-acid of 38° Tw., 0·066 per cent.; (b) drier acid of 2° Tw., 0·014 per cent. This proves that the AsCl_3 mostly volatilizes in the pan. As far as the sulphuric acid is concerned, Hjelt found, with the same Spanish pyrites, containing 0·91 per cent. of As, for each 100 parts of H_2SO_4 , in the

Chamber-acid	0·202	As, of which	0·040	as As_2O_5 .
Glover-tower acid	0·331	„	„	0·041 „
Gay-Lussac-tower acid ...	0·341	„	„	0·132 „
Acid of the last chamber .	0·019			

The higher proportion of the Glover-tower acid comes from the arsenic contained in the gas; the accession of arsenic in the Gay-Lussac tower is, of course, caused by the oxidizing action of the nitrous vitriol.

According to Davis (Chem. News, xxxvii. p. 155), in the Glover tower all arsenic acid is reduced to arsenious acid by the burners, and in the Gay-Lussac tower all is again converted into arsenic acid. This assertion is not in accordance with the analyses of Hjelt just quoted, nor with my own analyses, in which I always found both degrees of oxidation of arsenic at the same time.

Filhol and Lacassin found in three samples of “pure” commercial sulphuric acid, per kilog. :—1·2870 grm.; 0·5691 grm.; traces of As_2O_5 (Wagner's Jahresb. 1862, p. 212). Further estimations of arsenic in commercial sulphuric acid, according to Schnedermann, Kerl, Filhol, &c., will be mentioned below; those of Kuhlemann and Bräuning have already been given.

Of course, even with the same raw material, the arsenic in the sulphuric acid will vary, according to whether the gas-pipe leading from the burners to the chambers offers more or less opportunity for depositing arsenical flue-dust. When employing a Glover tower the acid contains rather less arsenic, because a large portion of it is deposited at the bottom of the tower in the shape of mud.

At the Freiberg smelting-works, where mixed ores containing from 2 to 2·5 per cent. of As are employed, about 97 per cent. of

the arsenic is condensed in the large and well cooled dust-chamber described p. 301, so that the acid contains mostly only 0·02 per cent. of As, only exceptionally up to 0·14 per cent., whilst formerly it amounted to 0·25 or even 0·5 per cent.

The acid made from the very pure pyrites found in some localities in the United States (p. 47) is, of course, free from arsenic.

Probably sulphuric acid intended for alkali or manure works is never submitted to any purification at all; and for most purposes where the acid ought to be free from arsenic, consumers employ the acid made from brimstone.

In most cases where sulphuric acid is employed a small percentage of arsenic is of no consequence—for instance, in superphosphate, or in sulphate of soda to be used for alkali- or glass-making. In the latter case certainly most of the arsenic passes over into the muriatic acid and can be traced there. When the muriatic acid is used for generating chlorine, the arsenic does no harm; for although it probably passes over, at any rate partly, into the chloride of lime, it will only occur in this as the insoluble and innocuous calcium arseniate. Much more harm is caused by arsenic in the sulphuric or muriatic acid which is employed in the food industries, for instance in the manufacture of starch-sugar, in the formation of molasses, for pressed yeast, for washing the regenerated char of sugar-works, &c. A. W. Hofmann has reported a poisoning-case in which bread was contaminated with arsenic by the use of arsenical muriatic acid along with soda to make the dough rise. It is unnecessary to speak of medicinal uses, since for them crude sulphuric or muriatic acid is never supposed to be employed.

But even for some purely technical uses arsenic in sulphuric or muriatic acid is not allowable:—on the one hand, for the preparation of certain colours, for tinning iron (sheet iron cleaned with arsenical sulphuric acid is here and there covered with spots of reduced arsenic, which will not take the tin coating,—see Gossage in Hofmann's Report by the Juries, 1862, p. 12); on the other hand, for the manufacture of preparations which serve for food or medicine, and into which a portion of the arsenic might pass over. To these belong tartaric, citric, phosphoric acids, milk of sulphur, sulphide of antimony, &c. Even in Doeberiner's lighting-machines arsenical acid must be avoided, since the arsenic-uretted hydrogen evolved in them would soon spoil the platinum

sponge. It has also been observed that ammonium sulphate made from ammoniacal gas-liquor by means of strongly arsenical sulphuric acid turns yellow, no doubt in consequence of the formation of sulphide of arsenic. It will be shown in the third volume, in describing Deacon's chlorine process, that arsenical sulphuric acid here seems to do great harm also.

In some cases, therefore, it is of importance for the producers of strongly arsenical vitriol to make it more saleable; and a number of methods of purification have been proposed with this object. None of them seems to produce an acid absolutely free from arsenic, but sufficiently so for all practical purposes. Bloxam (Pharm. Journal, [2], iii. p. 606), by employing his electrolytical method for the discovery of arsenic, found that all samples sold as "chemically pure" contained traces of it, and that acid absolutely free from arsenic cannot be obtained in any other way than from pure sulphur dioxide and nitric oxide in glass apparatus at a low temperature, avoiding all cork or india-rubber; the gases themselves must be evolved cold or at a very moderate heat.

The following methods have been employed for the separation of arsenic from sulphuric acid:—

(1) *Distillation* of the vitriol (Bussy and Buignet, Dingl. Journ. clxii. p. 454) is said to effect this purpose, even more completely than precipitation by sulphuretted hydrogen, provided that the arsenic is all present as *arsenic acid*, which remains entirely behind in the residue; if, however, arsenious acid be present, it is carried over with the vitriol. Since the sulphuric acid of commerce mostly contains arsenious acid, it is to be treated with nitric acid, in order to convert all the arsenic into arsenic acid; then the acid is to be mixed with a little ammonium sulphate (in order to destroy the nitrous acid) and distilled. In this case the arsenic is said to be removed more completely than by sulphuretted hydrogen or barium sulphide; at the same time the dilution of the acid, necessary in the latter case, is avoided. But the distillation of sulphuric acid is an operation not yet introduced at all on the large scale, and is not applicable for the purification of chamber-acid.

According to Blondlot (Compt. Rend. lviii. p. 76), the employment of ammonium sulphate is objectionable, because by an excess of it arsenic acid is reduced again. He therefore recommends heating the acid with peroxide of manganese or potassium permanganate. Bussy and Buignet deny that an excess of ammonium

sulphate reduces arsenic acid (Compt. Rend. lviii. p. 981). Marwell Lyte (Chem. News, ix. p. 172) says the statement of Bussy and Buignet, that arsenic does not distil over unless present as arsenious acid, is correct; but in order to obtain from the first a product completely free from nitrogen compounds, he destroys the latter by adding to the sulphuric acid $\frac{1}{4}$ to $\frac{1}{2}$ per cent. of oxalic acid, heating in a porcelain dish to 110° C. with continuous stirring, cooling down to 100° C., and adding potassium bichromate in the state of powder or as a solution in sulphuric acid, till the green colour has been changed to greenish yellow and the presence of free chromic acid is thus indicated. All the arsenic is now converted into arsenic acid; and on distillation a perfectly pure acid is at once obtained. Permanganate of potash performs the same service, but is more expensive.

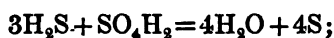
The process of Menzies, which will be described in the next chapter, is asserted to be at the same time a process for removing the arsenic in the shape of arseniate of iron, but it does so only very imperfectly, as we shall see.

(2) *Removal of the arsenic as trichloride.*—This boils at 133° C.; it is therefore completely volatilized on heating, long before the sulphuric acid has begun to boil: this process can be used without diluting the latter. With this object Otto and Löwe proposed heating the acid with common salt (Dingler's Journal, cxxxii. p. 205); Graeger, heating with barium chloride, because the action in this case is not so rapid (ib. clv. p. 236); Buchner (in 1845) recommended conducting a current of hydrochloric acid gas into boiling sulphuric acid and expelling the hydrochloric acid by heating in the open air. Bussy and Buignet have certainly proved that in this way acid free from arsenic cannot be obtained; but Buchner (Chem. Centralbl. 1864, p. 600) asserts that this comes from the presence of arsenic acid, and that an acid entirely free from arsenic is obtained by first reducing the arsenic acid contained in the vitriol by heating it with charcoal, when the sulphur dioxide evolved causes the reduction; this can also be done when introducing the current of hydrochloric-acid gas. If Buchner's statement is correct, the troublesome operation of distilling the vitriol is unnecessary. Schwarz (Wagner's Jahrbuch, 1865, p. 232) heats the acid for some time with 1 per cent. of common salt and $\frac{1}{4}$ per cent. of charcoal dust under a chimney with a good draught—which comes to the same thing, and appears to

be more convenient; but on carrying it out on the large scale, great difficulties arise from the fact that the process does not work with dilute acid, and that with the introduction of common salt into concentrated acid the glass retorts often crack. According to Tod (Liebeg's Jahresb. 1856, p. 292), if a current of HCl is introduced, heating to 130°–140° is sufficient, while if common salt be employed the acid must be heated to 180°–190° C., in order to expel the arsenic trichloride.

Selmi (Berl. Ber. 1880, p. 206) dilutes the acid with half its volume of water, adds some lead chloride, and distills off the first portion, in which all As is contained as AsCl_3 . Hager (Chem. Zeit. Rep. 1888, p. 234) repeats the same proposal, adding that the employment of chloroform, proposed as useful in this operation, may lead to dangerous explosions. The acid, after being decanted from the lead sulphate, is to be submitted to fractional distillation.

(3) *Precipitation of the arsenic as sulphide.*—This is the only operation carried out on a manufacturing scale which offers the additional advantage that, apart from the arsenic, several other impurities are precipitated (such as lead, antimony, selenium) and others are destroyed (such as sulphurous, nitrous, and nitric acids). Under all circumstances the precipitation must take place at a moderate concentration of the acid; too highly concentrated sulphuric acid is decomposed by sulphuretted hydrogen with separation of sulphur, according to the equation



the acid must therefore be in the state of chamber-acid, or, better, not above 106° Tw. When the arsenic is present as arsenic acid, it is much more slowly precipitated than when present as arsenious acid.

The simplest way might be thought to consist in generating the sulphuretted hydrogen within the liquid itself; and we shall first consider the methods and proposals made for this purpose.

(a) *Precipitation by barium sulphide.*—Proposed by Dupasquier in 1845, this process is said to be carried out practically at Chessy (Hofmann's Report by the Juries, 1862, p. 12); and it appears to be used at most of the French works where the acid is purified at all. In this case barium sulphate and sulphuretted hydrogen are formed, the latter being in the nascent state, and therefore acting

very energetically ; this process has, moreover, the great advantage of leaving nothing soluble behind in the acid. It has been objected that the barium sulphide must be pure and must contain no thiosulphate, since otherwise the well-known decomposition between H_2S and SO_2 , and separation of sulphur takes place ; this, however, is unfounded, because the barium thiosulphate likewise precipitates the arsenic in the state of sulphide (see below), and only an excess of it (which ought to be avoided in any case) would occasion the above-mentioned reaction.

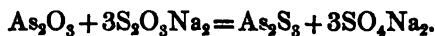
(b) *Sulphide of iron* may be employed in cases where the iron does no harm—for instance, for acid required in the tinning and galvanizing (zinking) of iron &c. Its application, however, is very limited.

(c) *Sulphide of sodium* is capable of much wider application, although it, too, introduces a foreign matter (sodium sulphate) into the acid ; this, however, is innocuous for most uses of the acid. It can easily be made by reducing sodium sulphate with coal ; and it must be added to the acid to be purified until no further precipitation takes place. The filtration of the precipitate will be described hereafter.

(d) *Crude calcium sulphide* (alkali-waste) can be used exactly in the same way as sodium sulphide, and with the same drawback of introducing some fixed impurities.

(e) Thomson (G. P. 6215, 1884) employs *ammonium sulphide* for precipitating arsenic and antimony, and at the same time destroying the nitrous compounds in chamber-acid. He then filters over finely divided lead, and concentrates in the usual manner.

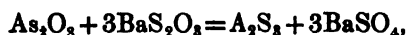
(f) *Sodium and barium thiosulphates* are very much recommended ; the latter is more expensive, but leaves nothing soluble in the acid. The following is the reaction which occurs :—



According to W. Thorn (Dingl. Journ. ccxvii. p. 495), the sodium thiosulphate is actually used in some works. Chamber-acid of 106°Tw. is heated to $70^\circ\text{--}80^\circ \text{C.}$, and the required quantity of the reagent, either in solution or as powder, is well stirred up with it. The arsenic sulphide is separated in flakes, which soon gather into lumps and sink down to the bottom of the tank ; the clear

acid is drawn off; and fresh quantities are purified in the same tank, until at last there is too much precipitate collected at the bottom, when it is removed and washed. The operation is very simple; and if an excess of the reagent is avoided, there is very little sulphurous acid evolved. In a particular instance, the average percentage of arsenic in chamber-acid of 106° Tw., before purification, amounted to 0·098 per cent., afterwards to 0·004 per cent. The purified acid contains from 0·03 to 0·04 per cent. sodium sulphate, which for most purposes is harmless.

In some cases the presence of sodium sulphate in the acid is objected to; especially when the strongest acid is to be obtained. It is therefore preferable to employ barium thiosulphate, which is easily obtained by mixing moderately concentrated solutions of sodium thiosulphate and barium chloride; most of the barium thiosulphate is precipitated in a crystalline form and is separated from the worthless mother-liquor on a vacuum-filter. The acid to be purified is heated to about 80° C., and is well agitated (which can be most readily done by a stream of air), the requisite quantity of barium thiosulphate is thrown in, and the temperature is kept at 80° to 100° till all the arsenic is precipitated. The reaction is:—



so that nothing soluble is left in the liquid. The mixed mud of arsenious sulphide and barium sulphate settles down very rapidly; it is separated from the acid by decantation or filtration and washed in order to remove most of the acid. Where the barium sulphate is of some value, it is easily recovered by boiling the mud with milk of lime, when the arsenic is dissolved, and can be re-precipitated from the solution for sale as "yellow arsenical glass," whilst the residue of barium sulphate can be submitted to the usual treatment for the manufacture of barium chloride. This process is actually carried out on a considerable scale, but it is not quite so cheap as the treatment with sulphuretted hydrogen, and does not seem adapted to acids containing a large quantity of arsenic.

(g) *Precipitation by sulphuretted hydrogen gas.*—This is the process principally carried out on a large scale. The older, now obsolete processes, used at Oker and Freiberg, are described and illustrated in our first edition, pp. 469 to 473. We will here give

only the results of Schnedermann's analyses of the acid before and after purification :—

(α) Impure acid contained in 10,000 parts—

Specific gravity.	Arsenious acid.	Lead sulphate.
1·832	11·86	3·74
1·837	13·19	2·85
1·836	14·21	5·21

(β) After purification, in 10,000 parts—

SO ₃	7749·10
H ₂ O	2243·54
PbSO ₄ (with traces of CuSO ₄) ...	1·72
Na ₂ SO ₄ and K ₂ SO ₄	1·35
CaSO ₄	0·58
FeSO ₄	2·91
As ₂ O ₃	0·31
H ₂ O ₂	0·49

It was perfectly free from nitrogen compounds. Subsequently, according to Kerl, acid has been obtained containing no more than 3·15 As₂O₃ and Sb₂O₃ together and 11·28 PbSO₄ in 100,000 parts.

According to official information, obtained by me from the Freiberg Mining Office, the original percentage of arsenic in the ores burnt there averages 2 to 2·5 per cent. As. 97 per cent. of this arsenic is condensed as flue-dust, about 3 per cent. gets into the chamber-acid, which before purification usually contains 0·02, but sometimes up to 0·14 per cent. As. It is employed in this state in the Gay-Lussac tower, or for the manufacture of superphosphate. All other acid is purified, as described below, and then contains only 0·0002 per cent. As₂O₃.

A complete description of the older precipitating-apparatus at Oker has been given by Knocke (Dingl. Journ. cliv. p. 185; Wagner's Jahresb. 1859, p. 145).

The more recent precipitating-process used at the Freiberg and a few other works is described at great length by Bode (Dingl. Journ. ccxiii. p. 25; Wagner's Jahresb. 1874, p. 259); the following is an abstract*. According to the former method the

* According to official information obtained by me the apparatus and processes described in the text were still at work in 1890.

vitriol had to be treated three times over before the precipitation was complete, and the evolution of sulphuretted hydrogen from stoneware pots was also very troublesome. When the plant had to be enlarged, the following new arrangements were made:—

1. *Generation of sulphuretted hydrogen.*—For this purpose, coarse metal is smelted, consisting principally of FeS, in which at the same time the silver contained in the crude ore is concentrated to the amount of one third of the original weight. The work is done in a blast-furnace with seven tuyeres; the mixture consists of

16.1 per cent. of lump pyrites, containing on an average 33 per cent. of sulphur.

0.3 „ „ roasted lump pyrites.

0.6 „ „ cinders from subliming arsenic sulphide, with 20 per cent. sulphur on an average.

83.0 „ „ lead slags, with about 30 per cent. silica.

100.0

Of this mixture 20 to 21½ tons are daily worked off, with a consumption of 3½ to 4 tons of coke (19 per cent. of the charge). The yield is 13½ per cent. of the charge as iron sulphide (80 per cent. of the ore); cost of smelting 3*d.* to 3½*d.* per cwt. of the charge. The furnace is minutely described in the original. The coarse metal is broken up into pieces of the size of a fist, and put into the sulphuretted-hydrogen-generators; these receive 4 to 5 tons at a time, which last 8 to 10 weeks. Then weak vitriol of 55° to 77° Tw. is added, such as is obtained in washing the arsenic sulphide; later on, the acid may go down to 32° Tw. Each apparatus daily receives 5 cwt. vitriol of 32° Tw. From 5 tons of coarse metal 7½ tons of green copperas are obtained, the manufacture of which from the weak lyes takes place in the usual manner. The generators are represented in figs. 240 to 246. They are wooden tanks A and B, made of 3½-inch planks, lined with lead and connected by a lead tube *a*. The tank A (5 feet 6½ inches square and 2 feet 2 inches deep) is charged with coarse metal after lifting off the cover, or through the man-hole *b*; an india-rubber washer is then put in, and the cover is tightened by thirty screw-bolts. The vitriol is run in through a pipe on the cover. B has also a cover, but without an india-rubber joint, as it has only to receive the

copperas-liquor forced over by the pressure of the gas in the washing-apparatus (figs. 245 and 246) and the regulating valves just as is the case with the ordinary laboratory apparatus. The tank A is very strongly bound with iron, which is all leaded over. Steam-pipes, *e*, prevent the copperas from crystallizing; *f* serves for running the liquor off. On the bottom of A radially-placed fire-bricks form a grate (fig. 242), upon which a lead sieve *g* is laid; and the coarse metal lies upon the latter. The lateral man-holes *h* permit raking out the residue containing silver. For each 5 tons of chamber-acid, on an average $1\frac{1}{2}$ cwt. of coarse metal is consumed.

2. *Precipitation of the arsenic.*—The chamber-acid of 106°Tw. is treated with H_2S without dilution or heating; the apparatus easily purifies 15 tons of vitriol daily by a single treatment. It is represented in figs. 247 to 253 (p. 647). It consists of a square tower of 5 feet 4 inches \times 5 feet $6\frac{1}{2}$ inches section, and 16 feet 3 inches available height, which is constructed in the well-known manner with a wooden framework and lead sides of 10 lb. to the square foot. The sulphuretted hydrogen enters at the bottom; the gas is carried along with it and the steam escape at the top. The tower is filled with 24 tiers of Λ -shaped inverted lead gutters, $5\frac{1}{2}$ inches high and as wide at the base, made of 10-lb. lead; the lower edges of the gutters have indentations of a tolerably small pattern (fig. 252). Owing to this, the acid cannot run down in jets, but only in single drops, which, in falling upon the next lower gutter, squirt about and present a large surface to the gas. In each tier there are nine gutters, so arranged that the passage between each two of them corresponds to the upper edge of the gutter in the next lower tier. They are 3 feet 3 inches long, and laid loosely on leaded ledges on each side, with 1 inch hold on the latter; their vertical distance is 7 inches; the distance between the tiers, therefore, $1\frac{1}{2}$ inch. The acid runs in at the cover *l* through lead pipes with funnels and regulating cocks, just over each of the lead gutters; there is a hydraulic lute and an oscillating bucket, the details of which are shown in figs. 252 and 253. The lead gutters should not be burnt fast in the tower, as lumps of arsenic sulphide occasionally get jammed between them. These can sometimes be melted and removed by letting in steam.

3. *The filtering and washing of the arsenic sulphide*, in the ordinary way, would be a very troublesome operation. At Freiberg

Fig. 240.

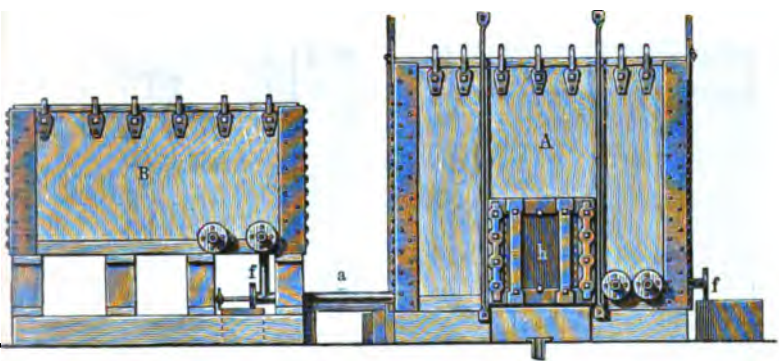


Fig. 241.

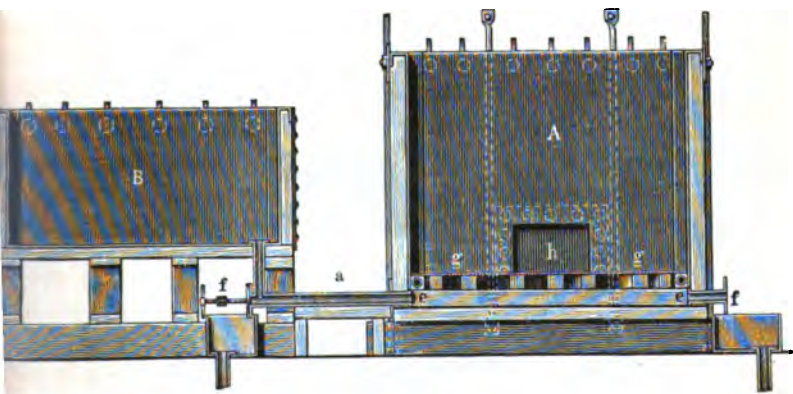


Fig. 242.

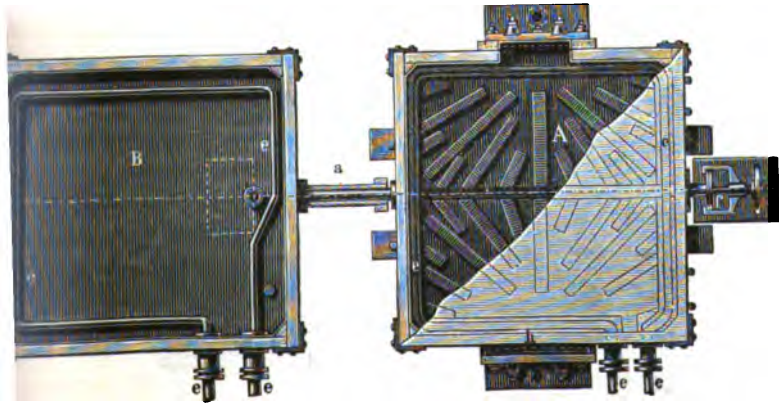


Fig. 243.

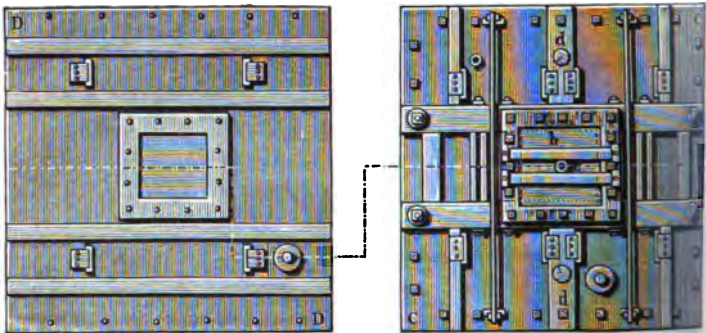


Fig. 244.

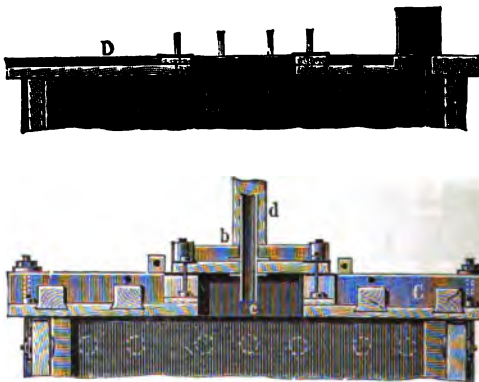


Fig. 245.

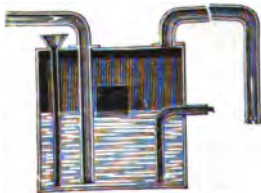
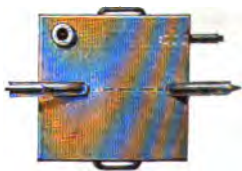


Fig. 246.



for this purpose an excellent apparatus is used, which is shown in figs. 254 to 256*. A is the vacuum-retort, B the filtering

Fig. 247.



Fig. 248.



Fig. 249.

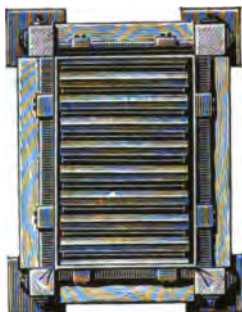


Fig. 250.

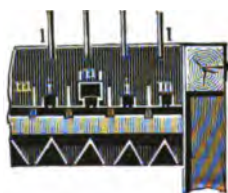


Fig. 251.

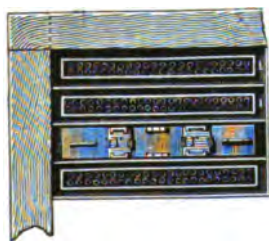


Fig. 253.

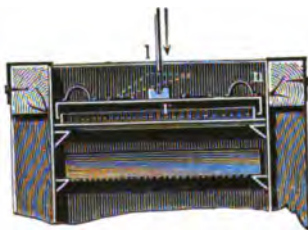


Fig. 252.

* Precisely the same principle has been applied in England for many years past for filtering the lime-mud in causticizing and for many other purposes.

and washing vessel. The former is a small, second-hand steam boiler of 1 foot 10 inches diameter and 5 feet 7 inches length. Steam is conveyed into it through *a* from a boiler; through *b* the air goes away along with the condensed water; and the cock then

Fig. 254.

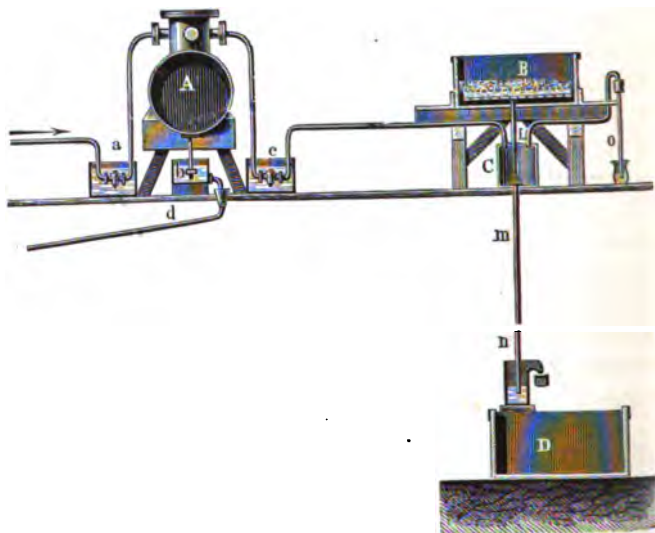


Fig. 255.

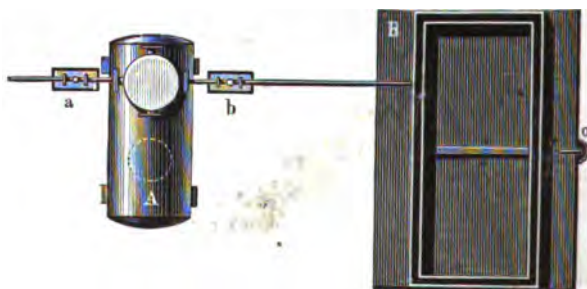


Fig. 256.



is only shut when steam has passed through for several minutes. Then *b*, and afterwards *a*, are shut, and the boiler is allowed to cool for some time in order to condense the steam. Then the cock *c* is opened, which connects the vacuum-retort and the space below

the filtering-layer in the box B. This box has already been filled with the acid to be filtered, whose level is always kept at the same height, lest any cracks be formed in the exposed layer of arsenic sulphide, through which air would enter and destroy the vacuum. By several times shutting *c*, opening *a* and *b*, driving out the air by steam and cooling down the boiler A, a vacuum of from 10 to 12½ lb. may be obtained. [Probably less steam and labour would be expended if an air-pump were used, as is done in England.] The same vacuum-retort [or air-pump] may work several filters, which may be filled, washed, &c. at will, since the cock *c* permits isolating every one of them.

The filters B are made of 2-inch planks, strengthened at the bottom at *e*, fig. 256, lined with lead, 4 feet 4 inches × 5 feet 7 inches section and 1 foot 10 inches high. A double pavement of acid-proof fire-bricks leaves a gutter, communicating with the burnt-on pipe *l*. This ends in an intermediate vessel C, whose cover is provided with connecting-tubes for the pressure-gauge, *o*, and the vacuum-retort, A, at *c*; *m* takes the acid to the receiving-tank *n*; but the pipe *mn* must be longer than the height of a column of water forced up by the atmospheric pressure, lest the acid should get over into *c*. Over the fire-bricks in B there is a layer *n* of broken-up quartz (fig. 256)—at the bottom, pieces of the size of a walnut—higher up, finer grain; over this there is a finely perforated sheet of lead, and on the top a layer of powdered arsenic sulphide; the whole filtering-stratum rises 11½ inches above the bottom of the vessel. Where the acid runs in, a piece of lead is placed so as to keep the top layer from being damaged. Every two or three weeks the layers *n* and *m* and the perforated lead plate must be taken out, and the quartz pieces as well as the arsenic sulphide must be rinsed in water. The whole plant requires several pressure-apparatus (acid-eggs) and a good air-pump.

At Oker the work is done very much as at Freiberg (Bräuning, *l. c.* p. 142); but here only that portion of the acid is purified which is not sold to large consumers, especially for superphosphate-making. It is thought best here to dilute the acid to 97°–100° Tw., and to assist the generation of sulphuretted hydrogen by injecting steam at the beginning.

An English patent of M'Kechnie and Gentles (No. 3229, 25th August, 1877) contains essentially the same process as is practised at Freiberg and Oker.

Leroy W. McCay (Chem. Ind. 1889, p. 371) proposes facilitating the precipitation of arsenic by H_2S , by conducting the operation at 100° under pressure and with agitation. [Such a process, excellent as it may be for the laboratory, is far too troublesome and costly for a manufacturing scale.]

Kupfferschläger (Bull. Soc. Chim. xliv. p. 353) dilutes the acid with its own volume of water, treats with SO_2 in order to reduce any arsenic or nitric acid to arsenious or nitrous acid, and then passes H_2S through, which causes all As, Pb, and Se to be precipitated. This proposal he repeats without any change whatever in 'Monit. Scient.' 1889, p. 1434.

The evolution of sulphuretted hydrogen, where no such matter is made at Freiberg is obtainable, can be produced cheaply with soda-waste, where an alkali-works is near. Hartmann (G.P. 9275) produces that gas by passing pyrites-kiln gas through a cupola-furnace filled with red-hot coke. When the temperature has gone down, the current of SO_2 is interrupted and air is blown into the coke till the heat has been got up again. Or else the impure SO_2 is mixed with the vapours of hydrocarbons and passed through a red-hot retort.

At an American works I found H_2S prepared for the above purpose from dilute sulphuric acid and sodium sulphide, manufactured for this purpose.

Purification of the Sulphuric Acid from Nitrogen Compounds.

Already, when treating of the purification of vitriol from arsenic, it has been stated that mostly by the same operation the nitrogen compounds are removed, and this is always the case when sulphuretted hydrogen is employed for that purpose. In most works, however, no such purification from arsenic takes place; and for most uses of the vitriol the small proportion of nitrogen compounds which they contain is so unimportant that their removal is not called for. In all cases, however, where sulphuric acid has to be concentrated in platinum apparatus, it must be purified as much as possible from absorbed nitrogen acids, as otherwise the platinum, as we shall see hereafter, would be much more strongly acted upon. Since this has been known, probably such purification takes place nearly everywhere, but by different methods.

1. *Purification by sulphurous acid.*—Payen has proposed a contrivance for this object. This is a cover over the first boiling-down pan, provided with partitions which force the gas to travel twice backwards and forwards, and below which the sulphurous kiln-gas circulates. Some, instead of this, use pans arched over. This apparatus, however, fulfils its purpose very inefficiently, because the contact between the vitriol and the sulphurous acid is very incomplete. This object can be attained perfectly in all works where a Glover tower is employed; in this the acid can be fully denitrated, and, moreover, some little sulphurous acid can be dissolved, in which case, as Scheurer-Kestner has shown (see Chap. XI.), it acts least upon platinum; but, unfortunately, the Glover-tower acid, owing to its large percentage of iron, cannot well be used for concentration in platinum stills.

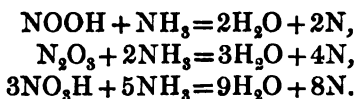
At some works they arrange a small preliminary chamber (tam-bour), in which there are bottom partitions open at opposite ends, so that the acid entering from the next (large) chamber has to travel a circuitous, long way before it arrives at the place where it is drawn off for use. This is done with the object of completely taking the nitre out of the chamber-acid and making it sulphurous, the fresh burner-gas acting upon this acid with full force. Such acid is then employed for concentration in platinum stills. The object of completely removing the nitre (and together with it the selenium) is still better attained by blowing kiln-gases by means of an injector right through the acid in a finely-divided stream, and allowing the deposit to settle down by running the acid in circuitous channels.

2. *Treatment with brimstone* has been proposed by Barruel. It is used in the shape of flowers of sulphur, which sometimes, according to Schwarzenberg, is put into boxes of stoneware, placed in the first pan, in which the temperature does not rise to the melting-point of sulphur, and in which the vitriol contains most water. Special care must be taken that no sulphur gets into the following pans, because strong hot vitriol is decomposed by sulphur with the formation of SO_2 , and for each part of S $6\frac{1}{8}$ parts of SO_4H_2 are lost. According to Bode ('Gloverthurm,' p. 3) this process is not efficient; so long as the brimstone is still in the state of powder, its action is very slight, although the lead is already being acted upon by the nitrogen acids. Later on, with the rise of temperature, the brimstone melts and rises in small drops to the

surface of the hot acid, whence it mostly escapes into the air as SO_2 .

3. *Treatment with organic substances.*—*Oxalic acid*, proposed by Löwe, has already been mentioned in the purification from arsenic. *Sugar* has been proposed by Wackenroder. Skey recommends agitation with *charcoal*, but only for dilute acid (Chem. News, xiv. p. 217). Olivier uses a little alcohol in the lead pans: ('Rapports du Jury international,' 1867, vii. p. 35).

4. *Ammonium sulphate* has been proposed with this object by Pelouze (Ann. Chim. Phys. lxvii. p. 52), and has been proved to be the best of all reagents. By this the nitrogen acids can be so completely removed that the vitriol is tinted red by the first drop of a solution of potassium permanganate. In this case nitrogen escapes, according to the following equations:—



This substance is now universally employed for acid to be concentrated in platinum stills. Under normal conditions 0.1 to 0.5 lb. of ammonium sulphate suffice for purifying 100 lb. of vitriol.

It appears as if the addition of ammonia was sometimes carried to a ridiculous excess; for Gintl (Wagner's Jahresb. 1880, p. 259) found, in so-called "chemically pure" sulphuric acid, 5 per cent. of NH_3 .

Pattinson (J. Soc. Chem. Ind. 1889, p. 706) recommends the treatment with ammonium sulphate for the sulphuric acid employed for generating carbonic acid in the manufacture of aerated beverages, as an extremely small quantity of nitrous acid (0.026 per cent. of N_2O_3) causes the beverage to be turbid, and destroys the pungency of the ginger essence &c.

Nörrenberg (Chem. Ind. 1890, p. 363) points out that the red colour sometimes found in commercial sulphuric acid of about 140°Tw . may be formed by the contact of that acid, when containing a slight quantity of nitrous acid, with iron tanks. The iron, acting upon the nitrous acid, generates nitric oxide, which is dissolved in the ferrous sulphate formed—thereby producing the red colour. Oxidizing agents discharge this colour by converting the ferrous into ferric salt, and the NO into N_2O_3 . Completely denitrated acid never assumes the red colour when kept in iron

tanks, nor does stronger acid ("rectified vitriol"), which has much less action upon the iron. The same colour may be produced in the small chambers or "tambours," sometimes placed before the first large chamber; here the sulphurous acid is still predominant, and iron is present as flue-dust, so that the conditions are present for the formation of a solution of NO in FeSO_4 . The main chambers, where nitre predominates, never show that colour, as here all the iron must be present as ferric sulphate.

Production of chemically pure Sulphuric Acid.

Hayes (Dingl. Journ. cx. p. 104) has proposed to add nitre to the vitriol of 152°Tw. , coming from the lead pans, sufficient for destroying the largest portion of any hydrochloric acid present, and for oxidizing completely the sulphurous and arsenious acids, then to destroy the nitrous acid &c. again by adding $\frac{1}{3}$ per cent. of ammonium sulphate—to add a little oxide of lead, to cool and settle in leaden vessels, and to cool the clear acid siphoned off in shallow lead pans down to -18°C. In this case the hydrate $\text{SO}_4\text{H}_2 + \text{H}_2\text{O}$ crystallizes out; the mother-liquor containing all impurities is decanted; the crystals are washed with pure acid, and then form square prisms sometimes an inch thick and $1\frac{1}{4}$ in. long. These are fused in clean lead vessels, and used as they are, or further concentrated in a platinum still. This process was intended to save the distillation; it has not been successful, however; for it is troublesome and yet does not produce a really pure acid. Exactly the same plan has been proposed by Tjaden-Möddermann (Zeitschr. f. analyt. Ch. 1882, p. 218; Fischer's Jahresb. 1882, p. 260).

The only plan for making perfectly pure sulphuric acid for pharmaceutical and analytical purposes is still *fractional distillation*, connected with such operations as previously remove the volatile impurities of the vitriol or convert them into fixed compounds. We have seen above how the arsenic and the nitrogen compounds can be removed. It is best to destroy the latter first by ammonium sulphate, and to convert the arsenious acid into non-volatile arsenic acid. It is safer, on account of the danger of spurting, first to remove both nitrogen compounds and arsenic by means of sulphuretted hydrogen; but then the acid must be much diluted previously. It never becomes absolutely free from arsenic

in this way ; it is therefore always preferable to employ brimstone-acid for rectification.

According to Nicklès, *hydrofluoric acid* is sometimes found in vitriol ; and it can be removed by diluting it with twice its bulk of water and heating it for 15 hours.

The fixed substances, such as iron, lead, copper, &c., remain in the retort on rectifying ; and in order to avoid contamination with organic substances, the receiver is changed when about $\frac{1}{20}$ part of the acid has come over ; the distillation is interrupted when only $\frac{1}{8}$ to $\frac{1}{10}$ of the acid is left behind. The portion distilling between these two limits is quite pure.

The distillation of sulphuric acid is a very disagreeable and even dangerous operation, on account of the strong *bumping* caused by the sudden development of large bubbles of vapour ; this is especially favoured by the lead sulphate separating. In such cases the retort is sometimes bodily lifted up, and of course smashed when it falls back upon its seat. The bumping must therefore be avoided as much as possible, for which purpose the following plans have been proposed.

Berzelius prescribed heating the retort more from the sides than from below, by placing a sufficiently wide sheet-iron cylinder upon the grate of the furnace, so that the bottom of the retort just fits into it ; the coals in the furnace then only heat its sides. In this case, however, the iron cylinder may act as a cracking ring ; and A. Müller (Polyt. Centralbl. 1860, p. 1069) therefore employs an iron pan, in whose bottom a special iron ring protects the retort-bottom from heating, whilst the remaining space of the pan round the retort is filled with fine cast-iron borings. Sometimes the retort is heated in an iron vessel just fitting it, which is generally filled with sand ; Reese (Dingl. Journ. clv. p. 395) puts ashes on the bottom, as a bad conductor of heat. Frequently, however, the retort is heated direct in a fire, and is merely protected by asbestos or by a paste of clay which is continued up to the curve of the neck, so that the vapour is prevented from condensing too soon.

In any case the retorts must be made of very good glass, free from knots, equally thick all over, and not too large ; the neck must be protected against draughts, and must not extend to the middle of the receiver, as the latter might be cracked by the hot drops of acid falling into it. It is neither necessary nor advisable

to cement the joint between the retort and the receiver, or to cool the latter, considering the high boiling-point of the acid; but it is useful to place a strip of asbestos between the neck of the retort and the receiver, in order to protect the latter against overheating at the point of contact.

The bumping is very commonly avoided by putting in substances which favour a regular evolution of vapour. For this purpose the following are useful:—platinum scraps or wire, for instance in the shape of spirals; bits of quartz, of porcelain, or of very hard coke. Pelloggio recommended a wide glass tube, drawn out to a fine point at the lower end, and reaching almost down to the bottom of the retort; through this the air can communicate with the interior (Polyt. Centralblatt, 1868, p. 392). Hager has tried this and found it useless. Dittmar conducts a continuous slow current of air through the boiling acid (see above, p. 114); this expedient has answered very well in my own laboratory.

When distilling about 1 cwt. at a time, it takes from 5 to 6 hours of moderately strong heating before the contents of the retort begin to boil; after 12 hours one twentieth has distilled off. The receiver is now changed; after 36 hours (counting from the commencement) the acid is distilled off within one eighth or one tenth, and the operation is stopped. According to whether the first change of receiver has been made a little sooner or later, acid more or less concentrated is obtained.

The following method is very much to be recommended, because the danger of handling such large quantities is hereby avoided. A small tubulated retort holding from a pint to a quart is employed; above this, a little to one side, a bottle of convenient size is mounted, provided with a glass tap, into which the sulphuric acid to be rectified is put, after it has been freed from all volatile impurities by previous heating. The distillation is now started in the small retort, which is about half filled, and into which a few scraps of platinum are put. Afterwards, by means of the glass tap and of a finely drawn-out glass tube, as much acid is allowed to run continuously from the stock-bottle into the retort as is distilling off. The operation may be continued till too much of fixed substances is accumulated in the retort. I have seen this plan at work on a small scale in English factories.

Pure sulphuric acid is now attainable in commerce at such a low price that it could not be produced by any of the just described

means. It is in reality manufactured from the weak acid distilling over in the production of rectified O.V. (comp. next Chapter), which is concentrated by evaporation in glass retorts, or preferably in a small platinum still, to the point required.

CHAPTER XI.

THE CONCENTRATION OF SULPHURIC ACID.

SULPHURIC acid, as obtained direct in the chambers (that is to say, from 106° to at most 124° Tw. strong), is sufficiently concentrated for many technical purposes; and where the acid is used up again for such purposes at the same works, its further concentration is, of course, out of the question. This is the case, for instance, with large industries having their own vitriol-works, with the manufacturers of superphosphate and of sulphate of alumina (concentrated lum). Even for making sulphate of soda from common salt it is possible to manage with acid of 124° Tw., although stronger acid is decidedly preferable; and in fact some alkali-makers (not so many now as formerly) work without any concentrating apparatus, making their chamber-acid as strong as possible. The want of concentrating apparatus formerly excluded the application of a Gay-Lussac tower; and such works certainly did not possess such a tower. With the introduction of the Glover tower the state of matters was changed, inasmuch as the manufacturers using this tower can concentrate all their acid to 144° or even 152° Tw. without any cost, and thus arrive at the same point as those who, not using that tower, concentrate their acid in lead pans. But since Glover towers are not universal, and since they are not suitable for all the uses of sulphuric acid (see p. 602), we must here describe the other concentrating-apparatus as well. These come into use especially where the strongest oil of vitriol is to be made, for which the Glover-tower acid is not very well adapted.

When boiling dilute sulphuric acid the escaping vapour consists most entirely of water, and contains very little sulphuric acid indeed. The acid remaining behind will therefore become more and more concentrated, without any material loss of acid, so long as 144° Tw. is not exceeded. Walter (as quoted in Bode's

'Glover Tower,' p. 17) found that the loss in concentrating vitriol in open pans up to 144° Tw. only amounts to 0.01 per cent. At the same time the boiling-point, which in the case of chamber-acid is about 147° C., gradually rises: that of acid of 144° Tw. is 200° ; that of acid of 152° Tw., 215° . Beyond this the boiling-point rises very rapidly, and finally becomes stationary at 338° C., at which point not yet real sulphuric acid (SO_4H_2), but an acid containing about 1.2 to 1.5 per cent. of water remains behind. In practice this limit is hardly ever reached; the heating is stopped when the remaining acid nominally shows 168° Tw.; often its real density amounts to only 1.830 or $1.835 = 166^{\circ}$ or 167° Tw. A table of the boiling-points of sulphuric acids, according to their dilution, has been given above at p. 135.

The way in which sulphuric acid is to be concentrated is modified, first, by the *material of the concentrating vessels*. From what has been said above (p. 144) it follows that sulphuric acid of 144° , or even up to 152° Tw., acts very little upon the lead, even when hot; and so long as the acid has not to be stronger than 144° Tw., *lead vessels* are nearly always used, which offer the advantage that they can be made of any size, and that when they are worn out they can be very easily melted up and the material used over again. It is not advisable to carry on the concentration in lead above 144° Tw., because at that point the lead is much acted upon; and in no case can lead pans be used beyond 152° Tw., both because in that case the boiling-point of the acid too nearly approaches the temperature at which the lead begins to soften, and because the acid then acts too strongly upon it.

The *quality of the lead* used for boiling-down pans is of great importance; this subject will be treated of in the Appendix, according to the most recent work done in that respect.

The further concentration of the acid must take place in vessels of glass or platinum, or in apparatus of peculiar construction, which will be described hereafter.

The concentration of sulphuric acid to 144° or to 152° Tw. is therefore always carried on in lead pans (apart from the Glover tower). These pans, however, may be constructed in very different ways. They may either be heated by a direct fire, and either from the top or from the bottom, or by steam, or by the waste heat of the pyrites-burners; and their construction differs accordingly, and will appear from the detailed description.

1. *Lead Pans heated from the top.*

This is the appropriate mode of firing when the purity and especially the appearance of the vitriol are of less moment than a saving in fuel and the accomplishment of a large amount of work. The acid in this case is, of course, contaminated by the flue-dust, and is always more or less stained by sooty matters, whence its English name, "brown vitriol," has arisen. These contaminations are quite harmless when it is used for decomposing salt, for superphosphate, and for many other purposes.

On the other hand the rate of evaporation with a fire from above is very quick, because, first, the hot gas is brought into immediate contact with, and thus can communicate its heat much better to, the acid than when the two are separated by metallic plates; secondly, the vapours formed thereby are at once removed by the draught—which, as is well known by experience, very much assists the evaporation. Moreover, fired from the top, the pans, if properly constructed, are much less acted upon than when fired from below; especially the danger of being burnt through from the workmen's carelessness is much diminished.

Concerning the loss of acid in evaporation no experiments have been published; probably it is somewhat larger than with pans heated from below. Hasenclever ('Berichte d. deutsch. chem. Gesellsch.' v. p. 504) mentions that these "evaporating-furnaces" have been done away with again at many works because the acid is easily overheated, and because much acid may escape with the fire-gas. In England, where the pans with top heat have been built in a more suitable manner than those mentioned by Hasenclever, they have never had to be removed for the reason mentioned by him.

According to the above, pans with top-heat are especially suitable for alkali- and manure-works or for acid to be sold to the latter, but less so for sale-acid for other purposes. They were formerly far more extensively used in England than pans with bottom-heat; but, like those, have mostly become superfluous where there are Glover towers. Such pans have been described by Godin ('Annales des Mines,' 1865, p. 344) and by me (Dingl. Journ. cci. p. 352). In any case the lead must be protected from direct contact with the fire; or at least the pans must be cooled in such a manner that the lead cannot melt. The first way of doing this

is to keep the pan always filled to the same level, and that near to its top, leaving only a sufficient margin to prevent any boiling-over. In ordinary work the acid is never drawn off altogether unless for repairs; but, the concentrated acid being heavier and sinking, it is continually drawn off from the bottom, and fresh acid is continually run in at the top, as long as the concentrating process goes on. Even then the empty portion of the pan has to be protected, especially at the fire-bridge; and, in many English works, for this purpose formerly a lead pipe was burnt on all round, through which ran a continuous stream of cold water. This contrivance cannot be highly recommended, because the pipe soon gets leaky. Moreover the raising of the water costs something; and therefore the following arrangement is preferable.

Fig. 257.

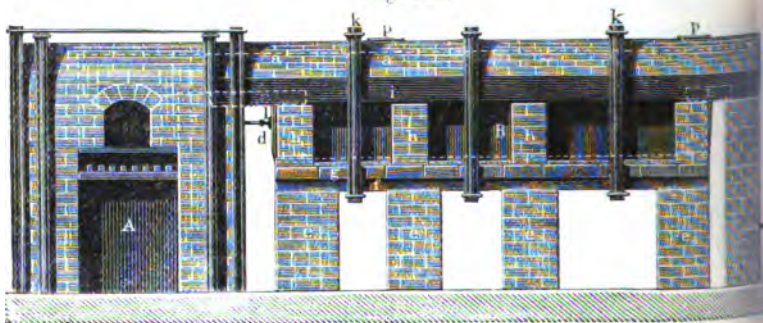


Fig. 258.

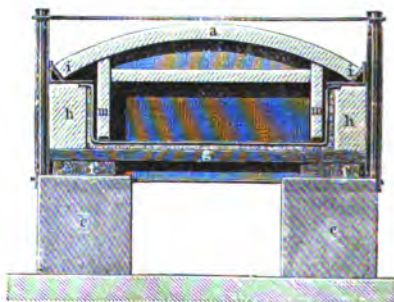
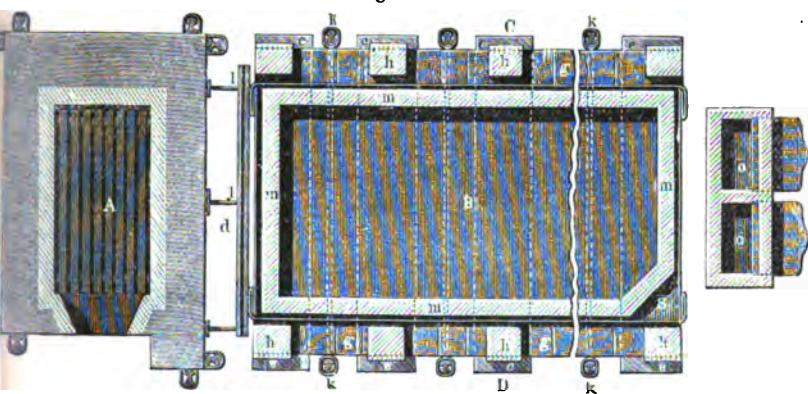


Fig. 257 shows a front elevation, fig. 258 a cross section, and fig. 259 a plan, of a pan with top-heat. The fireplace, A (2 ft. x 4 ft.), is built up quite independently; its only connection with the

Fig. 259.



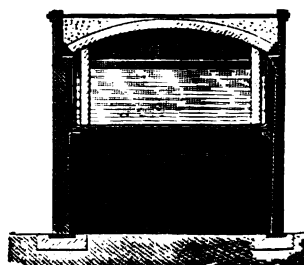
pan B is by the arch *a*, and the fireclay slabs *c*, 2 feet long, lying on the fire-bridge, *b*; the slabs *c* have a 6-inch hold on *b*; and as the space *d* between A and B is 1 foot wide, they project 6 inches into B. The fireplace in A is here shown as a plain grate; it might, of course, be more rationally constructed, and at some works it is replaced by a gas-producer. The air-channel, *d*, prevents any injurious influence of the heat of the fireplace on the pan, and we need only regard the flame itself in that respect.

The pan B is always made of a single sheet of lead, weighing from 15 to as much as 30 lb. per superficial foot; the corners are not made by cutting out, but by folding over, as shown plainly in fig. 259. Since such stout lead cannot easily be bent cold, along the line marked out for the folding a small fire of shavings is made, of course taking care to avoid melting the lead; the lead then softens sufficiently to be bent with ease. The pan is placed on brick pillars, *e e*, standing quite free, so that the space between them and below the pan is accessible at any time. On the pillars strong wood beams, *f f*, are laid; and across these 3-inch planks are placed close together; they are covered with a thin layer of sand, on which the pan itself is set. The pillars and beams project on each side 10 inches beyond the pan itself, and thus support small brick pillars, *h h*, 9 inches square, not quite touching the lead, and connected together at the top by cast-iron girders, *i i*. These have an angular section, and serve as springers for the arch *a*, which is thus quite independent of the pan. In themselves the pillars, *h h*, are much too weak to bear the side pressure of the

arch; but this is kept up by the binding-rods, *k k*. The upper margin of the lead pan is bent round at a right angle, and jammed in between the pillars, *h h*, and the girders, *i i*; in this way the sides of the pan are kept stiff. Next to the fireplace, where the pan becomes hottest and most readily gives way, it may be protected by iron rails and stays, *l l*.

A neater, but rather dearer, plan is this:—Instead of the brick pillars, *e e*, there are cast-iron columns provided, carrying, about halfway up, brackets, upon which metal plates for supporting the pan-bottom are laid. The columns are connected at the top by metal girders serving as springers for the pan-arch, and are kept together by bracing-rods. Fig. 260 will make this plainer.

Fig. 260.



The proper protection of the pan from the fire is brought about by the dry wall, *m m*, built up all round within the pan, of the best, hardest, acid-proof firebricks or stoneware slabs. At the long sides the wall reaches up to the arch; at the fire-end it only reaches to the upper margin of the pan, and there carries the projecting fireclay slabs, *c*; at the chimney-end there are similar slabs, *n*, reaching up to the down-draught, *o*. The wall, *m m*, stands about 1 inch off the pan-sides, and has openings at the bottom, so that the acid can circulate freely. It is evident that the fire can nowhere touch the lead itself; and, moreover, the pan is also protected outside by the cooling action of the air; so that it cannot possibly melt, or even soften. If the sides of the pan are to be stayed against bulging out, it should be done by open grids of cast-iron, which do not prevent the lead from being cooled. The greatest danger of giving way is still left at the fire-end, to which, certainly, great attention must be paid. In the arch there are man-holes, *p p*, and an inlet-pipe for acid, whilst the strong acid is drawn off by a siphon from the end *s*, left free by the arch; it is still better to attach to the bottom of the pan an overflow-pipe which rises to its top, and whose mouth can easily be narrowed according to requirement. The pan is preserved better if the fresh, cool acid runs in at the part nearest the fire-bridge, whilst the strong acid is taken away from the opposite end of the pan, where it is coolest. It is always

too hot to be used directly; and therefore it is run into shallow lead coolers, stayed by iron or wood frames, of which one is being filled whilst the contents of the other are being used. If the acid should not run off sufficiently strong, either the fire is increased, or the supply of weak acid is diminished, or both.

The width of the pan is dependent upon that of the sheet-lead; if for the sides about 17 inches each are allowed, about 4 feet 11 inches generally remain. The length is always much more considerable, rarely below 20 feet, but sometimes as much as 33 feet. The longer the pan, the better the fire is utilized. The consumption of fuel is always much less than for pans with bottom-fires; Bode estimates it at from 10 to 12 per cent. of the strong acid. The repairs of a properly constructed pan of this kind are much less than those of a pan with bottom-heat (as it always is in analogous cases); and the work done is much larger for an equal area. A pan of 4 feet 11 inches width by 33 feet length was sufficient, in my experience, for boiling down 80 tons of acid of 144° Tw. per week, from chamber-acid of 116° – 124° Tw.

Clough ('American Patent, Official Report,' i. p. 495, iii. p. 166) has proposed a similar apparatus for concentrating the vitriol up to 170° Tw. His pan was protected from the fire, inside by a wall, and outside by cold water contained in an iron jacket. This can hardly be put into practice, because the loss of acid vapours would be too great, and the pan would not stand the wear and tear, in spite of the water-jacket.

2. *Lead Pans with bottom-heat.*

These pans are mostly made of much smaller size than those with top-heat; the essential reason of this is the different wear and tear which they suffer according to whether they are more or less exposed to the fire; moreover the concentration in this case is very regular, the pans always being arranged in sets, so that the weak acid flows in at one end of the set and runs over from one pan to another till it runs off sufficiently strong at the other end of the set, in order to be used up or sold, or to be further concentrated in platinum vessels. Sometimes, however, long pans made in one piece are used, especially in England. In that case the first part, nearest the fire, is protected by an arch, the larger part of the pan-

Fig. 261.

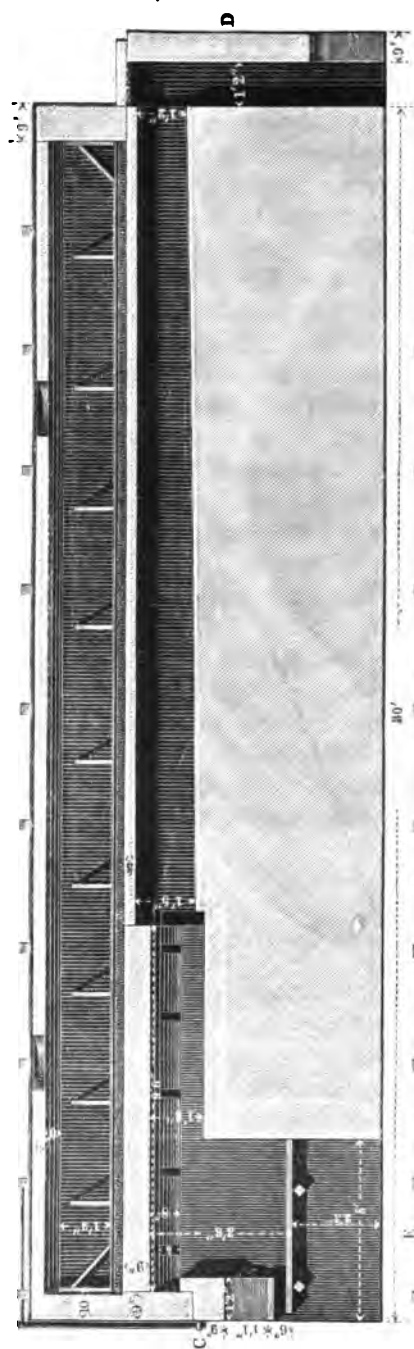
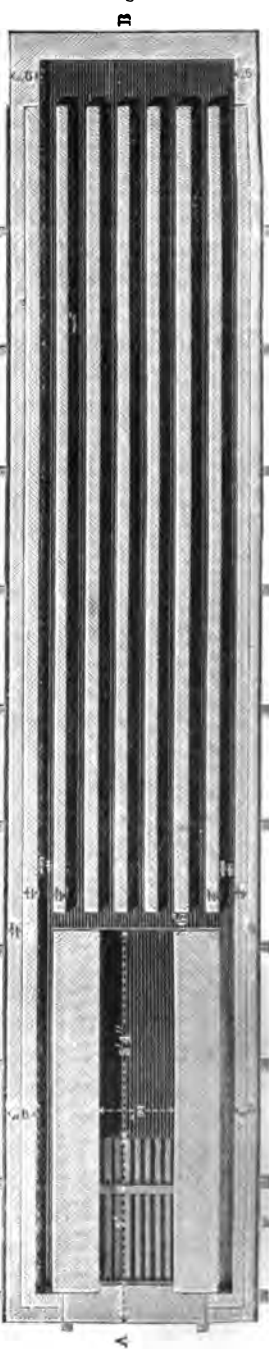
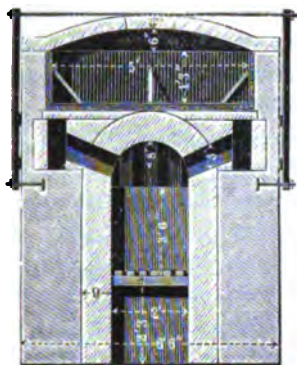


Fig. 262.



bottom behind this by fire-clay slabs or metal plates, as shown in figs. 261 to 263.

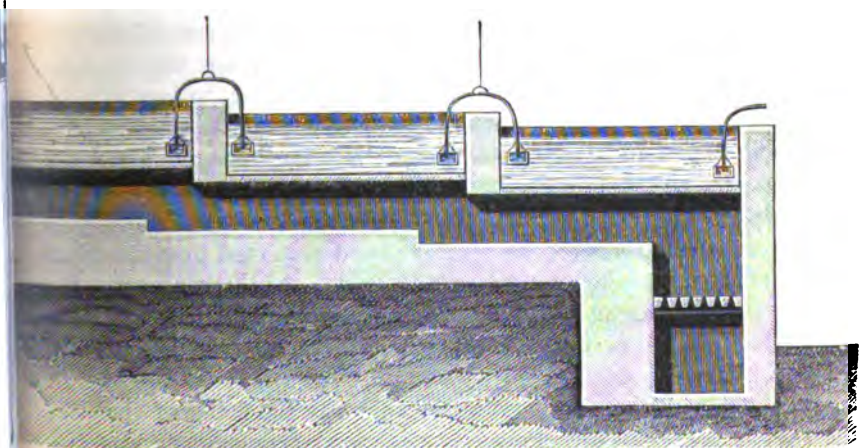
Fig. 263.



The metal plates are sometimes covered by a thin layer of sand, in order to communicate the heat evenly to the pan ; but this greatly hinders the heat-convection. The pan is stiffened inside by iron stays covered with lead ; and it is covered by an arch to carry off the vapours into the open air or into the chambers—the latter rarely.

On the Continent small pans are very generally used, of 5 to 7 feet length and width, and from 12 to 16 inches depth, of which

Fig. 264.



from four to six form a set. They are made of 15- to 18-lb. lead, mostly by bending up the sides and folding over (not cutting out) the corners. Sometimes such pans, instead of being made of sheet-lead burnt together, are *cast*, about $\frac{3}{4}$ inch thick. They are in that case exposed to the fire directly, without interposing iron plates. This plan cannot, however, be recommended. Such cast pans, being much thicker, are dearer than those made of sheet-lead; and they are much more liable to have unsound places, which are very soon eaten through. They are often set in steps, each pan about $2\frac{1}{2}$ inches lower than the preceding one, as shown in fig. 264; in other cases, however, they are placed with their bottoms at the same level, but are made of different depths—the pan which receives the weak acid being the deepest (16 inches), and each following one a little lower, the last pan (for strong acid) coming down to 12 inches. In this way the acid can also flow from one end of the set to the other. At the Oker Works there is a long pan divided by partitions into seven compartments of equal height and level; the fire-grate is in the centre of one side; and the flame first passes in the centre to the back, and then returns at both sides to the front of the pan.

The acid is sometimes carried over from one pan into the next by continuously acting cup-siphons, as seen in fig. 264. But as such siphons frequently cease to act in consequence of air getting in owing to the slow current and the small difference of levels, there ought always to be an overflow-pipe provided to prevent the pans from running over. It is even preferable to replace the siphons altogether by overflow-pipes, which take the acid from the bottom of one pan and allow it to run on to the top of the next one; but this arrangement requires the work of a very good plumber, to last without continual repairs. The chamber-acid is constantly running into the first pan in a regulated stream; and the strong acid runs off from the last pan without any further interference, the supply being so regulated that the proper strength is obtained.

The pan-bottoms are always stayed and protected from the direct action of the fire by cast-iron plates, which are thicker at the fire end than further off—say, decreasing from 2 inches down to $\frac{1}{2}$ inch. Frequently the first pan, below which the fireplace itself is built, is protected by an arch.

Opinions differ on the point, in what way the firing of the pans should be arranged. Formerly the usual arrangement was that

of putting the fireplace under the strong pan, and allowing the fire to travel towards the weak pan, which receives it last of all. In this case the greatest heat exists where it is most required, since the concentration of the strong acid is more difficult and its boiling-point higher, and since the fire-gas ultimately comes into contact with cold acid. When the pans are set terrace-fashion, the fire takes its most natural direction, viz. upwards.

Practice has, however, decided for the opposite plan, namely, arranging the fireplace under the weak pan, so that the strong pan is furthest from the fire. In this case the strong pan, which is otherwise worn out very quickly, suffers hardly more than the others, and the evaporation still goes on at a satisfactory rate, although there may be a little more fuel used than with the old arrangement, which is undoubtedly more rational as an evaporating plant, but less adapted to the special needs of this case.

Bode cites the temperature and strength of the acid in a set of six pans, where the fire travelled in the same direction as the acid, viz. :—

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.	5th pan.	6th pan.
a. Temperature 25°	112°	150°	160°	148°	145°	143° C.
Strength 110°	118	120	128	134	140	144 Tw.
b. Temperature 24°	110	145	156	145	142	142 C.
Strength 110°	118	118	126	134	140	144 Tw.

Here the hottest pan is the third ; so that the fire is badly utilized. According to his experience this set required 20 parts and upwards of coal to produce 100 parts of acid of 144° Tw. ; whilst in the set figured below, where the fire meets the acid, only 15 to 16 parts of coal were used (on the average of several years). For each ton of strong acid, in 24 hours about 20 superficial feet of pan-bottom may be reckoned ; the whole set, therefore, furnishes 6½ tons every 24 hours.

Bode gives the temperatures and strengths of the acid during concentration in pans with the old style of setting as follows :—

Set of four pans :

Acid running in.	1st pan.	2nd pan.	3rd pan.	4th pan.
Temperature 20°	52°	78°	120°	138° C.
Strength 106°	141 Tw.

Set of three pans heated by the pyrites-burners :

Acid running in (heated previously).	1st pan.	2nd pan.	3rd pan.
Temperature 70°.....	105°	128°	147° C.
„ 57°.....	92	106	125 C.
Strength 106°	144 Tw.

According to Hasenclever, it is well to regulate the working of the pans by thermometers, in order to avoid any risk of damaging them.

Figs. 265 to 268 represent the set of pans designed and constructed by Bode, where the fireplace is outside, in order to save the

Fig. 265.

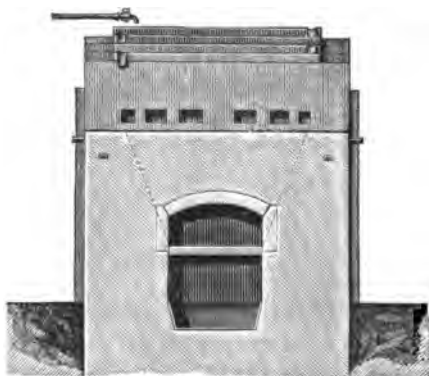


Fig. 266.

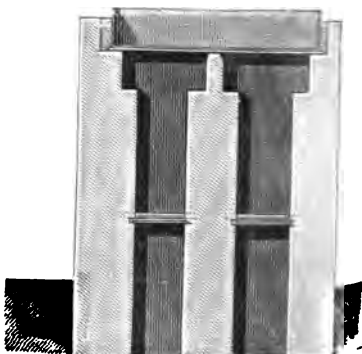
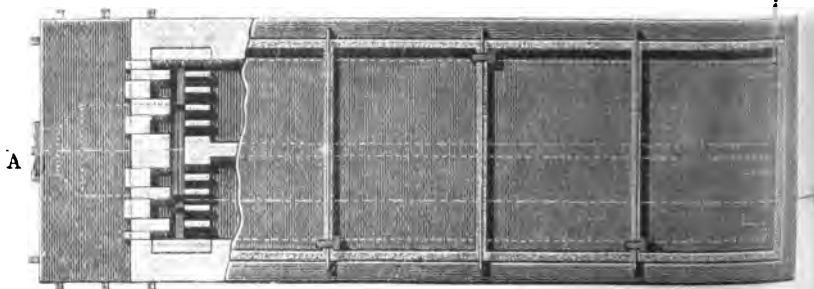


Fig 267.



first pan. The second plan designed by Bode, and represented in figs. 269 to 272 seems still better. In this there is no outside fire-

Fig. 268.

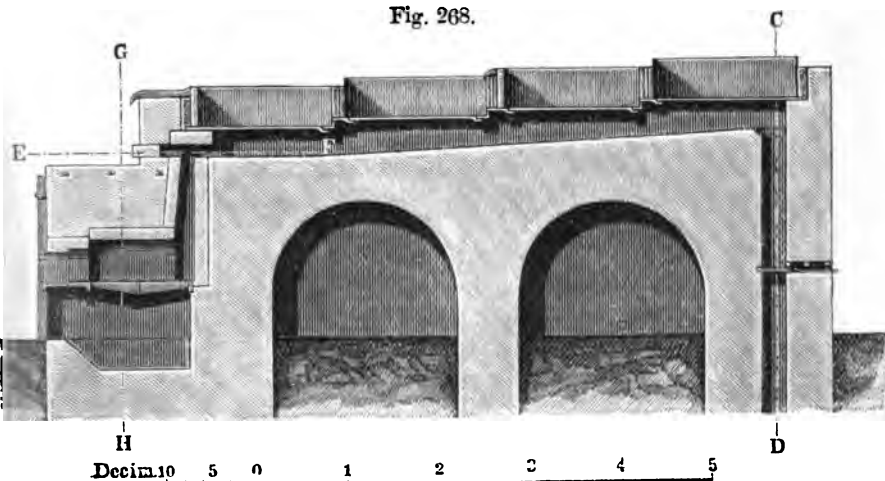


Fig. 269.

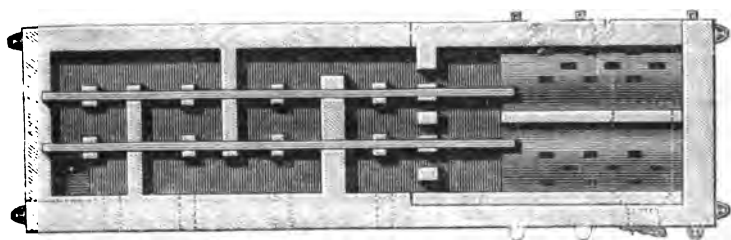


Fig. 270.

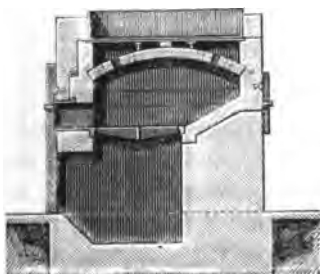
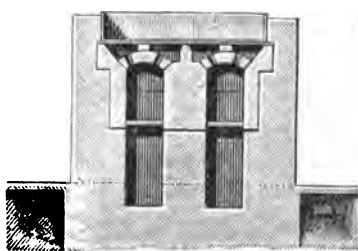
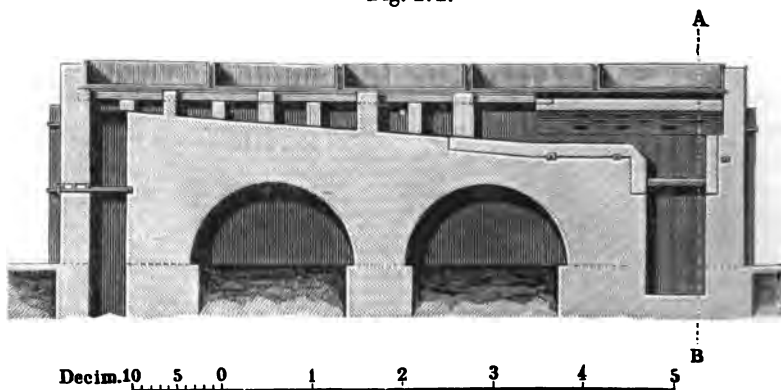


Fig. 271.



place, but a protecting arch. From this, by means of a pan-area of 118 superficial feet and a fire-grate of $6\frac{1}{2}$ superficial feet, 5 tons of strong acid could be produced every 24 hours, with a consumption of 12 to 14 per cent. of Silesian coal. Figs. 269 and 271

Fig. 272.



show a modification, in which a Fairbairn's double fireplace is used. In all of these the strong pan is placed over the fire, as usual formerly, whilst at the present day the order would be reversed.

According to Scheurer-Kestner (Wurtz, 'Diction. de Chimie,' iii. p. 159), four pans, 6 feet $6\frac{1}{2}$ inches by 3 feet 11 inches each, permit the concentration from 109° to 152° Tw. of sufficient acid to produce 3 tons of concentrated acid daily, with a consumption of no more than half a ton of coals.

Bode calculates the cost of erecting a concentrating-apparatus like that shown in figs. 269 to 272 at £150, and that of keeping it in good working order at 12 per cent. per annum. The cost of the concentration itself, reckoning coals, wages, and wear and tear, in four actual cases, amounted to from 2s. $3\frac{1}{2}$ d. to 2s. 8d. per ton.

3. Lead Pans fired by waste heat.

In works where there are platinum apparatus for making acid of 170° Tw., the fire of these can never be so far utilized that the waste heat could not be employed for heating lead pans; and this is actually done in most practical cases.

Much more generally applicable, and quantitatively more effi-

cient, is the utilization of the waste heat of pyrites- or sulphur-burners for concentrating chamber-acid. Where there is no Glover tower (which utilizes that waste heat in a different and even more thorough manner) the above process is most rational, since here also the same operation that produces the concentration of the acid, fulfils another useful function, that of cooling the burner-gas before it enters the chambers.

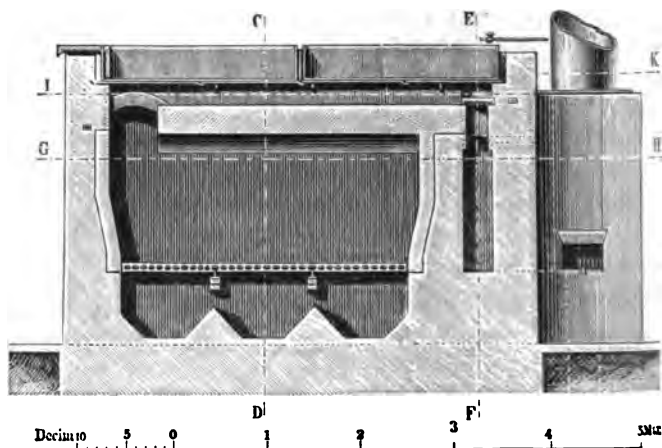
The pans used here are generally made exactly like those for concentrating with bottom-fires. They are mostly placed on the pyrites-burners themselves ; they must not, however, be set directly upon the burning pyrites, nor even with merely a metal plate between, but must be separated from it by a brick arch. In most cases there is immediately over the burners a gas-flue, serving at the same time as a dust-chamber, on the top of which the acid-pans are placed (see the diagrams of Malétra's burners, pp. 253 and 254). Sometimes, if there is any fear of leakage from the pans into the burners, they are not placed over these, but upon a continuation of the gas-flue. Hasenclever even advises building a second gas-flue, to be used during the time when the pans have to be repaired. The heat of the kiln-gas will not thus be turned to account so well as if the pans stood directly upon the burners ; and the danger of leakage into the burners can be avoided by providing the metal plates, on which the pans rest, with a flange all round and an outflow for any acid collecting in it, like those used in nitre-ovens. Leakages occur also less easily where the pans are very shallow, so that the depth of acid is only a few inches. But, on the other hand, it has been noticed that sometimes, especially in the case of poorer ores, the pans on the burners withdraw too much heat from these to be conducive to good burning.

Whilst at some places such pans on the top of the burners concentrate all the chamber-acid from 112° to 114° Tw., at others this cannot be done, and a little extra coal is required for completing the concentration.

The diagrams, figs. 273 to 279, represent pans designed by Bode, along with the pyrites-kilns used by him. The apparatus shown here belongs to a set of chambers of 40,000 cubic feet capacity ; and each burner receives daily 16 cwt. of Westphalian pyrites containing 42 per cent. of sulphur. The grate of each burner has a surface of $34\cdot4$ square feet ; the grate-bars are elliptical, 3 inches by $1\frac{1}{2}$ inch, each of them movable ; the arch is 4 feet 4 inches

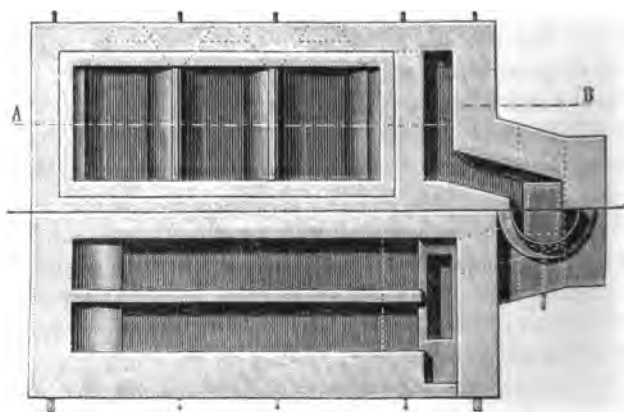
above the grate, with a spring of 7 inches. The diagrams show how each burner can be cut off separately. The pans are 6 feet

Fig. 273.



3 inches by 4 feet 2 inches by 1 foot 2 inches, made of sheet-lead weighing $8\frac{1}{2}$ lb. per superficial foot. They supply daily, when $1\frac{1}{2}$ ton of pyrites is burnt, altogether 2 tons 5 cwt. of acid of 144° Tw. (that is to say, 5 cwt. in excess of the make of the chambers); but as at the same time from 15 to 18 cwt. daily have to be evaporated for

Fig. 274.



the Gay-Lussac tower, the excess causes no inconvenience. Each year three new pans used to be put in, a pan never being left until

Fig. 275.



Fig. 276.

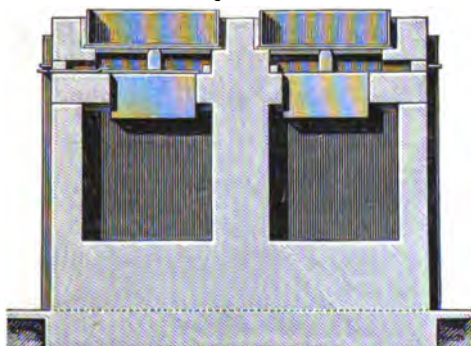
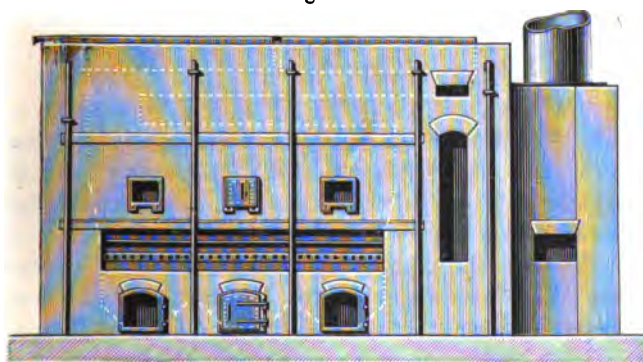


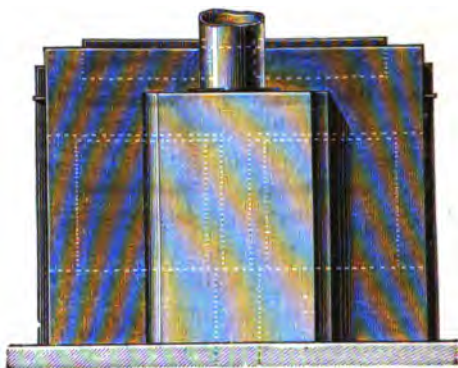
Fig. 277.



Decim. 10 5 0 1 2 3 4 5 Mtr

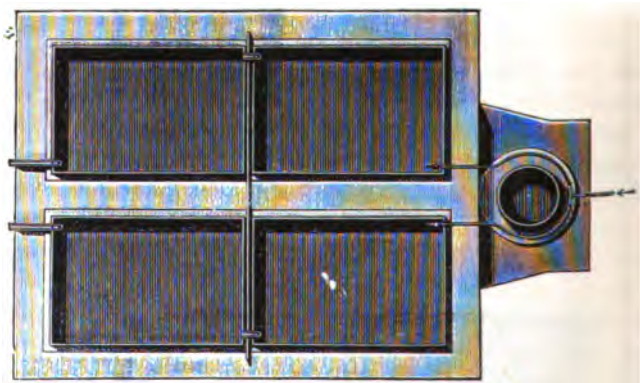
actually burnt through, but replaced as soon as the lead has

Fig. 278.



become too thin—a plan most decidedly to be recommended in

Fig. 279.



every case. The renewal only refers to the strong-acid pans; those for weak acid are hardly injured at all. The former are therefore much better made of thicker lead, say 30 lb. to the superficial foot, in which case they last for about two years.

The cost of concentration with such pans only amounts to a small fraction of the wages of the burnermen, in addition to the expense of renewing the pans; Bode calculates it, for a special case, at 4½d. per ton of strong acid; for less-favourable cases he estimates it at 6d. to 9d. per ton.

Several manufacturers and managers, even of high standing, have quite recently assured me that it is irrational to concentrate the acid on the top of the burners, because the trouble and incessant repairs caused by leakages are believed to be far worse than the expense of heating the pans by a separate fire. To this I must oppose that I know of a goodly number of works where all the pyrites-kilns are provided with pans placed on the top, and where this arrangement has been at work for many years (in a special case I can speak of 17 years) without giving any trouble whatever. This is proof conclusive that the troubles from leakages complained of are caused by a wrong setting of the pans, or else by keeping too deep a layer of acid in them (the latter being a very important circumstance). Where they are not placed directly over the kilns, but over the gas-flue (even this flue is itself on the top of the kilns), and where they are properly protected below by metal plates and a thin sand bed, they stand as long as may be desired, provided that only a shallow layer of acid is kept in them. Indeed, it may be said that such an arrangement of utilizing part of the heat of the pyrites-kilns, and allowing the other part to act in the Glover tower, is decidedly the best and cheapest plan, where the acid is required of purer quality than can be obtained from the Glover tower; the latter then acts much more as a denitrator than as a concentrator, and the acid produced in it is principally used for the Gay-Lussac tower, the surplus only being used or sold for other purposes.

With *brimstone-burners* it is equally possible and altogether rational to employ their heat for concentrating sulphuric acid. In this case the burners are not covered with an arch, but with 1-inch cast-iron plates, and shallow lead pans are placed immediately above these. Such an arrangement is distinctly shown in Dr. Stahl's sulphur-burners (*suprà*, p. 197); in H. Glover's burner (p. 201) it is combined with a platinum dish. This partial utilization of the heat of the gases does not at all prevent their employment for working a Glover tower. I have seen this combination carried out in several places in America, where the Glover tower denitrates and concentrates all the acid destined for working the Gay-Lussac tower, while the acid for sale is concentrated up to 140° Tw. on lead pans placed on the top of the brimstone-burners. The Glover acid in these cases still issues about 150° Tw. strong, and 126° to 30° C. hot.

4. Concentrating-pans heated by high-pressure steam in lead coils.

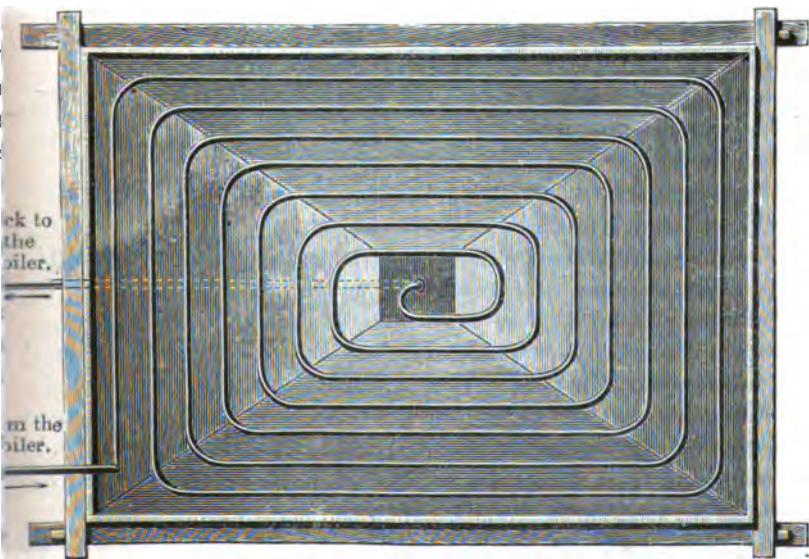
According to Hasenclever (Ber. d. deutsch. chem. Ges. v. p. 504), the first idea of concentrating sulphuric acid by means of indirect steam is owing to Carlier, the Manager of Messrs. Curtius' chemical works at Duisburg. After several trials at that works they now use wooden tanks lined with lead, 13 feet square, on the bottom of which lie two lead coils, each of 150 feet length, $1\frac{1}{4}$ inch bore, and $\frac{1}{4}$ inch thickness of lead, for conveying steam of 45 lb. pressure. The bottom of the pans is shaped like a truncated pyramid, for the purpose of more easily running off the condensed water; so that the tanks are 2 feet deep in the centre, 1 foot deep at the sides. The two ends of each steam-coil are connected with a lower-placed steam-boiler, into which the condensed water continually flows. When the acid has arrived at 140° Tw., it is run into a leaden tank, through which a lead coil runs; the fresh chamber-acid runs through this coil; and, in cooling, the strong acid gets a preliminary heating. With the above apparatus 5 tons of strong acid can be obtained from chamber-acid of 160° Tw., every 24 hours; by the consumption of 9 cwt. of coals. The steam-boiler requires only as much fresh water as gets lost through leakage at the flanges &c. It is advisable to place a wooden hood over the steam-tank, to prevent any danger from acid being splashed about in case of a steam-pipe bursting. Owing to the low temperature, no acid at all is evaporated; the process is very cleanly, and economical as to consumption of fuel and labour. This Report of Hasenclever is fully borne out by Bode. Hasenclever (Hofmann's Report, 1875, i. p. 185) states the corrosion of lead to be equal to 0.44 lb. of lead per ton of acid. The steam-pipes are mostly acted upon in the places where they dip into the acid, because the dust accumulating there raises by capillarity some acid above the level of the remainder, and this becomes too highly concentrated by evaporation. Since a lead jacket has been burnt to the steam-pipe at the place in question, the above drawback is no longer observed.

Figs. 280 and 281 represent a similar apparatus, after Bode's 'Gloverthurm,' p. 27. The tank here measures 10 feet 6 inches by 14 feet 9 inches at the surface, 1 foot 4 inches depth in the centre, 1 foot at the sides, is heated by steam of 37 lb. pressure

and supplies in 24 hours 5 tons of acid of 114° Tw. with a consumption of 10 cwt. of Silesian coal. At some works Bode found a consumption of only 8 cwt., at others, however, from 15 to 18 cwt. of coal for the same quantity of vitriol.

The steam-coil must have a valve both where it enters and where it leaves the pans, which should admit of being closed from a distance in case of the coil bursting. Both the coil and the return-pipe for condensed water (for which a steam-trap should be provided) must be so laid that the water cannot cause a stoppage anywhere. The lining lead weighs from $6\frac{1}{2}$ to 10 lb. per superficial foot. The whole cost of concentration by these pans, including labour, wear and tear of the pan-lead and of the steam-boiler and coils (using 9 cwt. of coals for 5 tons of vitriol), is calculated by Bode at *1s. 8d.* to *1s. 10d.* per ton of strong acid.

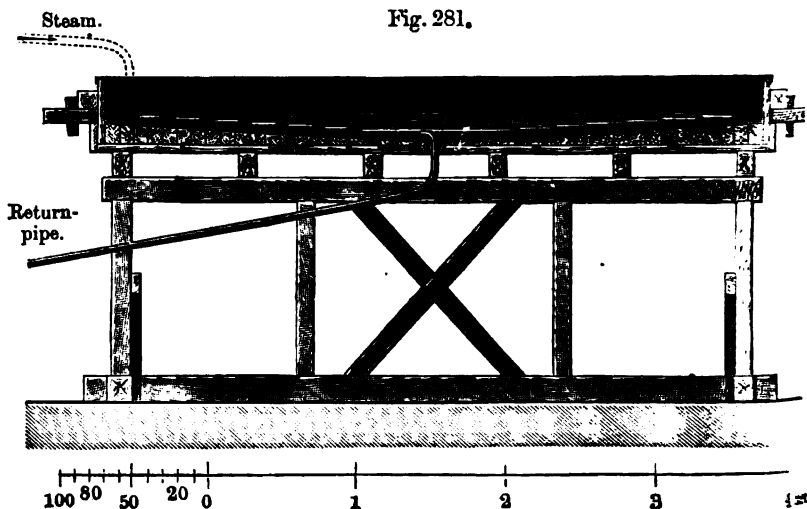
Fig. 280.



It is very important to place the outlet for acid in such manner that the steam-coil remains completely covered when running off the acid, and is never exposed to the air, which would greatly injure the lead. After a year's work the steam-coil ought to be replaced by a fresh one, even if not showing any outward damage.

Some manufacturers are afraid of running the condensed water back into the boiler, lest the latter should be damaged by any

acid getting into it, or even caused to explode ; in such cases the above-mentioned larger quantity of coals is used. Bode points out that there is no danger of acid getting into the steam-boiler, because in case of the steam-boiler bursting the steam blowing off will prevent the acid from entering the boiler. The return-pipe must not end below the water-line, but in the steam-dome.



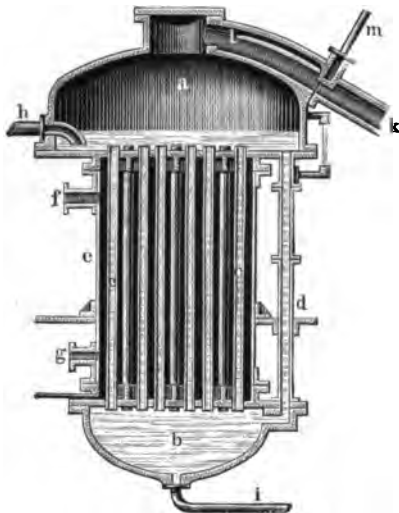
Dr. Stahl recommends employing steam of no more than 30 lbs. pressure, in order to reduce the danger of bursting pipes to a minimum.

The process of concentration by steam certainly furnishes the purest acid, and was formerly considered cheaper than the other plans, excepting the Glover tower or the pans placed on the pyrites-burners. It has been introduced into several German works, but latterly the reports on the economical working of that plan have not been so favourable as formerly.

Several new steam concentrating-apparatus for sulphuric acid have been introduced in connection with ice-making apparatus, all of them founded on the principle of the multi-tubular boiler. We mention of these the apparatus of Kux (G. P. 31,277), fig. 282. The upper part *a* and lower part *b* are connected by many lead pipes *c c* ; through these and the outside pipe *d* the acid circulates. The whole system is surrounded by a shell *e*, into which steam is introduced through *f*, the outlet being at *g*. The thin acid is introduced

t *h*, the concentrated acid flows away at *i*; pipe *k* takes away the vapours, and a water-pipe *m* with an inner pipe *l*, perforated by many holes, condenses any acid carried over.

Fig. 282.



Egells (G. P. 31,620) describes a very similar apparatus, in which the tubes are placed in a horizontal direction, and special precautions are taken against any sagging of the tubes *c*. Kurtz (G. P. 37,713) employs lead pipes provided with inner iron pipes. A combination of a leaden pan with evaporating-worms placed sideways of it forms the subject of a patent of the International Vacuum-Eismaschinenverein (G. P. 38,015; Fischer's Jahresb. 1887, p. 508).

Fontenille (G. P. 37,713) forces hot air through dilute sulphuric acid flowing over perforated plates.

5. Concentration to 144° Tw. in Platinum Vessels.

Concentration in platinum dishes, in Faure and Kessler's apparatus. The inventors state that 7 parts of coal suffice for obtaining 100 parts of vitriol of 144° Tw. from vitriol of 106° Tw., of which quantity 4½ to 5 parts of coal may be deducted if the steam be used for the acid-chambers. The same might be done in any other plan; but it rarely is done, because too much air is carried along with the steam. According to Bode, in reality 10½ parts of

coal are used, the warm water being utilized for feeding a boiler. This system, applied to concentration up to 144° Tw., does not seem to be able to compete even with the steam-pans, let alone the burner-pans or the Glover tower, least of all if the cost of plant be considered.

The last Concentration of Sulphuric Acid.

We have seen that we cannot carry on the concentration in lead pans beyond 150° or, at the outside, 152° Tw., the latter not without a somewhat strong action upon the lead. In the Glover tower it is possible to go rather further, as its lead is protected by the lining so as to be acted upon very slightly: the acid does not come into contact with the lead, but only with the flints, bits of pottery, &c., and arrives at the bottom with a temperature of about 130° C.; so that even the bottom of the tower, which is made very strong, is not sensibly acted upon. In fact those manufacturers (being the majority) who work the Glover tower with hot gas from rich ores, and get their chamber-acid up to 120° – 124° Tw., regularly attain a concentration of 152° Tw.; and in some cases even 156° or 160° is reached. The latter is the exception, and already dangerous to the tower; if it were not so, the concentration by hot kiln-gas in the Glover tower (of course modified to some extent) would be the cheapest plan for the last concentration of the vitriol, because then the escaping gas goes into the chambers and is not lost at all.

Concentration beyond the point attainable in lead pans or in the Glover tower is a much more difficult task, involving incomparably more expense than the first concentration. Since the attempts to concentrate the vitriol up to 170° Tw. by means of cooled lead pans with top-heat (Clough), or by a vacuum (Keller, De Hemptinne), or in towers filled with pebbles and heated directly by heating-gas (Gossage), and others have not been successful, and since cast iron is only available beyond the point to which "rectified O.V." is brought in ordinary work, recourse must still be had to apparatus made of glass or platinum, of which the former have the drawback of very restricted size and great liability to breaking, the latter that of being very costly without being proportionately durable. These circumstances make their application both expensive and troublesome (comp. below about porcelain).

By far the largest quantity of vitriol is used of no higher

strength than is attainable in lead, mostly even rather weaker. For making sulphate of soda—that is, ultimately soda ash—the acid is never taken stronger than 144° Tw., generally only 140° Tw. The English manufacturers as a rule dilute their Glover-tower acid down to this point with chamber-acid; or they only make as much acid of 52° in the Glover tower as is required for working it, and they keep the remaining acid weaker by running more chamber-acid through the tower. For superphosphate the acid is mostly employed even in a weaker state; and this, along with the sulphate of soda, swallows up most of the total quantity of vitriol made. In the great majority of cases sulphate-of-soda and superphosphate works make their own sulphuric acid, and, of course, do not concentrate it beyond their own requirements.

Touching the acid made for sale, however, a circumstance has to be considered here which in many cases induces the manufacturer to incur the great expense and trouble of concentrating the vitriol as highly as possible, even in cases where the consumer, not requiring it of such strength, must himself dilute before using it. This is the greater expense of package and transit for the same weight of real acid in the dilute as compared with the concentrated state. Apart from those cases in which completely concentrated vitriol is asked for on account of the smaller cost of package and transit, or from old habit and ignorance, there are many cases in which the consumer is really obliged to employ an acid of the highest possible strength:—for instance, the purification of rape-oil; that of benzol, paraffin, and other mineral oils; the refining of gold and silver; the production of nitro-cellulose, nitro-glycerine, nitro-benzene, and other nitro-compounds; that of sulphonic acids, for instance those of benzene and anthraquinone for the manufacture of resorcin and alizarine; for dissolving indigo, and many other purposes. In many cases an acid containing from 93 to 94 per cent. of SO_4H_2 will do; and often that which is sold as acid of 170° Tw. does not contain any more, and really ought to show only 166° Tw. ($=1.83$ sp. gr.)*. For making nitro-compounds especially, however, an acid of greater strength is required, containing 97 or 98 per cent. of SO_4H_2 ; even this cannot show more than 1.840 sp. gr. at 0° , or 168° by a really true hydrometer, unless it is very impure and contains much foreign matters.

* Recently more correct hydrometers have been used, and the quotations are no longer made for acid of 170° Tw. (which does not exist in the pure state), but 168° Tw.

This "extra-concentrated" acid can also be made in platinum vessels, but at the cost of dissolving much more platinum than ordinary rectified oil of vitriol. In this way it is possible to get up to 98 per cent., or at most 98.5 per cent. These high strengths, as we shall see below, can also be made in cast-iron vessels, which are not available below 96 per cent. For some purposes an acid of as nearly as possible 100 per cent., that is, mono-hydrated sulphuric acid, is required. This used to be made by adding some fuming oil of vitriol to ordinary sulphuric acid; but it is much better made by freezing, as we shall see *infra*.

Manufacture of ordinary rectified Oil of Vitriol.

It has already been mentioned that either *glass* or *platinum* vessels are used for the last concentration of sulphuric acid. Which of these two materials is to be preferred to the other has been a matter in dispute for a long time; nor is it settled now, both systems being largely employed. Formerly, before the platinum industry was developed, *glass retorts* were the only available apparatus, and those could only be had of comparatively small size and bad quality. They were also mostly set in "galley furnaces," a double long row of retorts being heated by a fireplace at one end: thus the retorts near the fire were, of course, much more heated than the distant ones, and were much sooner finished, or even overheated before the distant retorts had been sufficiently fired. Each retort was either put into a metal pot, with some sand between, or protected from the direct flame by a covering of clay and horse-dung. Both owing to the inferior quality of the retorts and the unsuitable setting, there was always much breakage, combined not only with the loss of acid, but also with the sudden evolution of suffocating vapours. The cracking of the retorts was especially induced by a cold draught getting at them; and since in that case the workmen had to save themselves instantly from the vapours by leaving the room, frequently the cracking extended to all the retorts. Besides, the expenditure of time, wages, and fuel in this process was very great.

There was always, therefore, an inducement to discover some other material than glass; and the only practicable metal, *platinum*, was at once applied, in spite of its high price and difficult management, as soon as Wollaston's process of welding spongy platinum

into ingots and plates was made known. The first still appears to have been made in 1809 at London; it weighed 423 ounces ('Chem. News,' xxxviii. p. 43). At that time platinum stills, weighing from 66 lb. to a cwt., were made, holding 4 to 6 tons of vitriol, and costing from 40,000 to 50,000 frs. (£1600 to £2000). This large sum did not deter manufacturers from using platinum for the last concentration of vitriol, because they convinced themselves at once of the large amount, facility, and safety of the work of concentration that could be carried on in them, and because they thought (although erroneously) they could reckon upon such apparatus lasting almost for ever.

The platinum vessels made by Wollaston's process were often porous and unsound, so that vitriol oozed through; besides, blisters and rents frequently appeared in them, which had to be soldered up with gold. The platinum stills themselves, therefore, gave much dissatisfaction. This, however, has been much diminished since Ste.-Claire Deville taught the melting of platinum in large masses by an oxygen-gas blowpipe in furnaces made of quicklime, casting perfectly sound ingots of it weighing 2 cwt., and, further, to solder the joints with platinum itself instead of gold, analogous to the burning of the lead chambers. In London this process was first applied in 1860. Since then the stills have been much more durable and at the same time cheaper, although the monopoly of the raw material by the Russian Government, and the unavoidable concentration of the platinum-industry in very few hands, still tend to keep the price of platinum apparatus at a very high figure.

When, however, attention was drawn to the fact that platinum itself is gradually acted upon by sulphuric acid (see below), and that thus the large capital expended on the stills not only involved heavy permanent charges for interest, but would have to be gradually written off altogether, and when, on the other hand, great improvements were effected in the manufacture and treatment of glass retorts, the latter came to the fore again, and began to drive platinum vessels out of the field, more especially in England. In 1862 Hofmann mentioned, in the 'Report of the Jury,' that in Lancashire the use of platinum retorts had almost ceased; at that time about $\frac{1}{10}$ of all the vitriol in England was concentrated in glass. In France and Belgium glass retorts existed along with platinum; but the latter held a wider ground; and in Germany it

was almost exclusively used. In 1868, the 'Official Report of the International Jury,' vii. p. 34, states that concentration in glass was then very rare (in France).

In order to meet the competition of glass, the platinum-works made efforts to construct the stills more durable and more cheaply, and they have indeed recovered a portion of the field previously lost. Later on they were urged on to renewed efforts in this line by the combination of platinum and lead employed by Faure and Kessler, which has again receded into the background.

At the present time the matter stands thus:—Both glass retorts and platinum stills are in use, some of the latter made according to the old and others according to the new system. The glass retorts are mostly used for the rather less concentrated acid, containing 92 to 93 per cent., the platinum stills for the more concentrated acid, 94 to 96 per cent.; in a few cases both are employed at the same works for these different objects. The glass retorts, however, are almost entirely confined to England, and in Lancashire are almost exclusively used; on the Continent, platinum vessels are used nearly everywhere but in a few places exceptionally well situated for obtaining glass retorts—for instance, Montpellier, where, according to Payen, a retort of 18 gallons capacity only costs 1·6 franc, whilst at Paris and most other industrial centres the price is 6 francs. Since such a retort holds a little over $1\frac{1}{2}$ cwt. of strong vitriol, and on an average can be used five times, furnishing altogether 8 cwt. of vitriol, the retorts for 1 ton of acid at Montpellier cost 6 francs, at Paris &c. 15 francs. In America both glass and platinum apparatus are used.

If the enormous rise in the value of platinum which has taken place in 1890 should prove to be permanent, the use of glass retorts, and perhaps also those of porcelain, cast iron, &c. (see below), will receive a fresh stimulus.

Concentration in Glass Retorts.

The shape of glass retorts now in use for concentrating oil of vitriol was introduced by Chance Brothers, of Oldbury, near Birmingham, who make them at their glass-works at Smethwick. They are shown in fig. 283 (this, together with figs. 284 & 285, is taken from Roscoe & Schorlemmer's 'Chemistry'). These retorts consist of two separate parts, viz. a large bottle *a*, with a neck at

CONCENTRATION IN GLASS RETORTS.

Fig. 283.

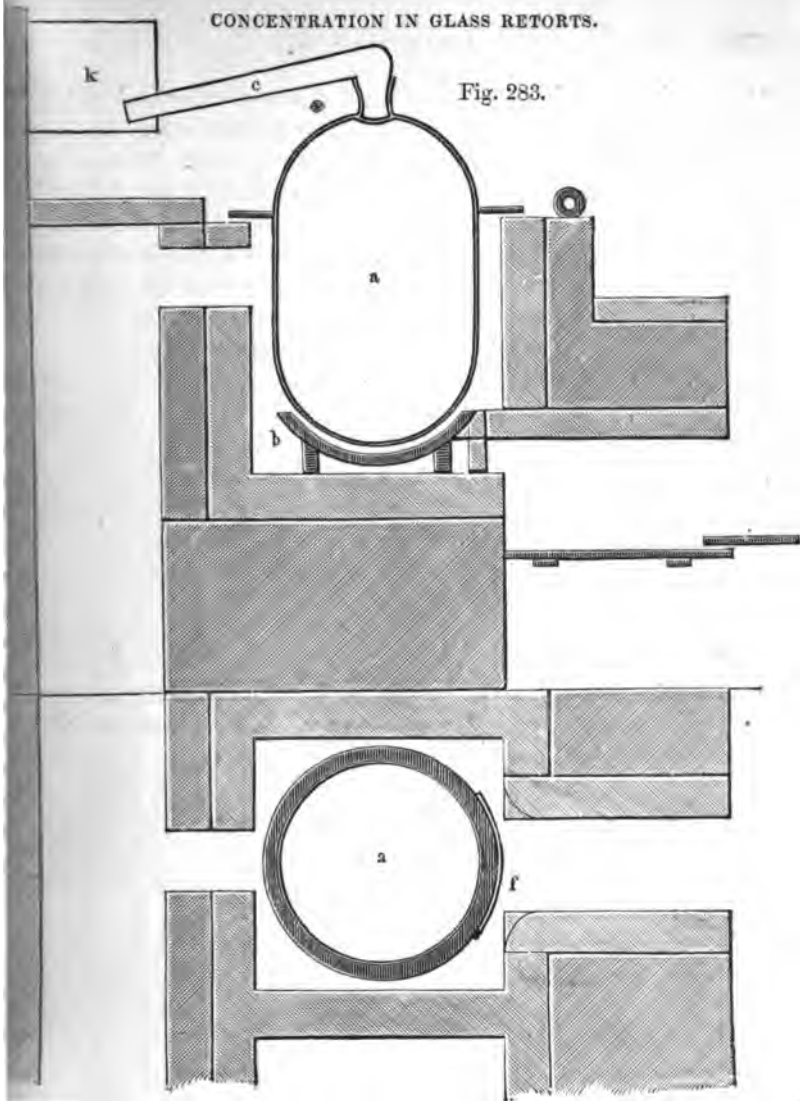
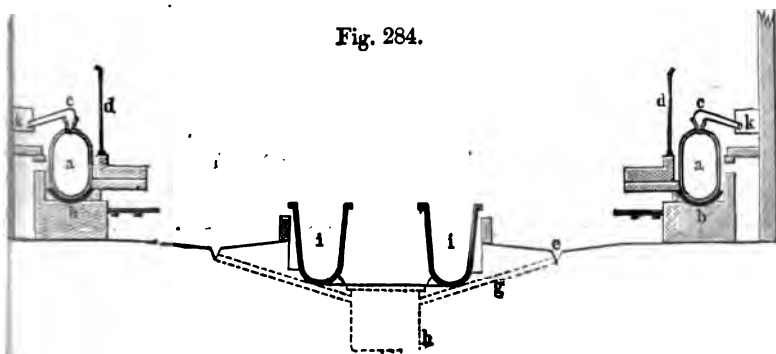
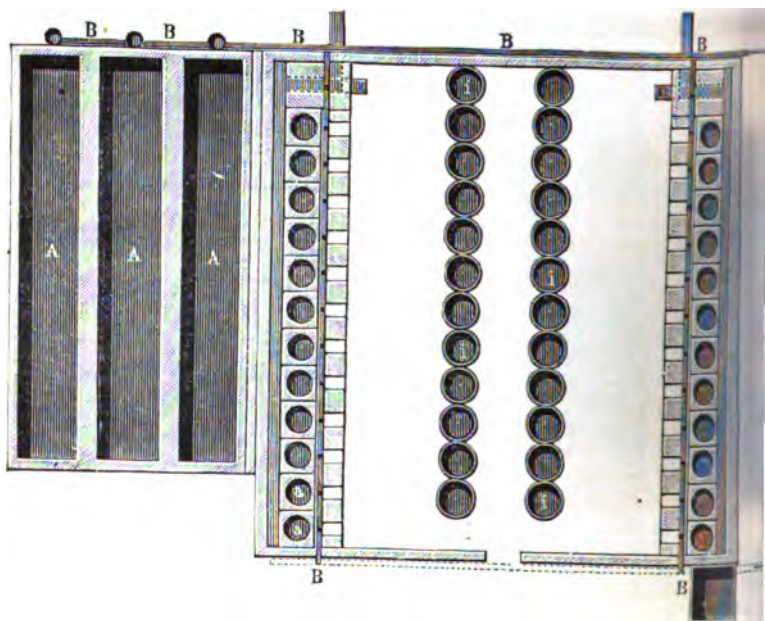


Fig. 284.



the top, into which fits a loose head *c*, whose other end enters an aperture in a lead pipe or tunnel *k* running all along the retort house, and ultimately connected with a chimney. The bottles are blown of thin glass, as evenly as possible, about 3 feet high from the bottom to the top of the neck and 1 foot 9 inches diameter. They rest on a flat metal sand-bath *b*, and are protected from direct contact with the flame by the round fire-clay slab *f*. In the pipe *k*, which conveys the condensed acid vapours to a collecting-tank, there is always some suction produced by the chimney draught at the other end; therefore the head *c* needs no cement to connect it with the bottle, as no vapours can get out, only air being able to enter. This is very important, as the head *c* has to be taken off and put on every day. The above-mentioned suction has also this effect, that retorts may be at work with cracks in their upper parts, provided such cracks do not reach down to the level of the acid in the bottle.

Fig. 235.



A number of retorts are always grouped together as seen in fig. 285, where A A A are boiling-down pans, from which the main pipe B takes away the hot acid of 144° Tw. On this

Fig. 286.

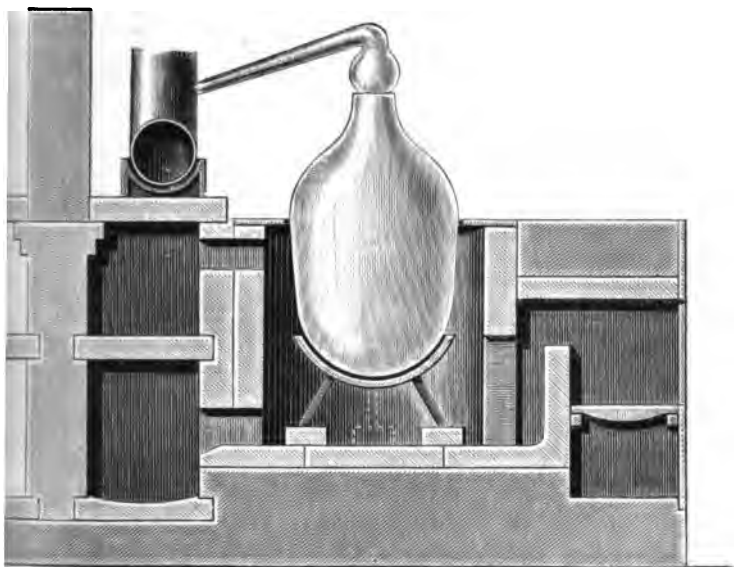
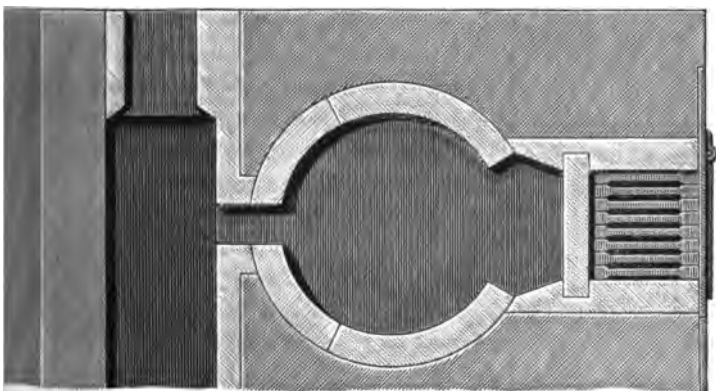


Fig. 287.



fixed long thin lead pipes *dd* (fig. 284), which are bent down at the bottom, in order to fill the single retorts. *ii* are cooling-pots for the strong acid drawn off, from which the carboys are filled. The floor is made a little sloping, so that in the case of a retort breaking the acid runs into the gutter *e*, and from this through pipe *g* into the tank *h*.

An accurate plan (to scale) of a retort-setting is given in figs. 286 & 287; this will be intelligible without further explanation.

The retorts (in number from 20 to 50) are placed in a separate house, the temperature of which is kept constantly at from 25° to 30° C., it being provided with tight-fitting windows and double doors; only one door is opened at a time, the other being shut, so that no draught (the chief cause of the bottles cracking) can enter. A retort-house with 24 retorts can turn out about 5 tons per diem.

The work is carried on in this way. The distillation goes on all day long, and is finished in the evening. During the night the acid cools down to some extent; in the morning the retort-heads are taken off and the acid is drawn off by siphons of platinum or thin lead tubing with a very narrow orifice. The siphon is filled with cold acid, the narrow opening closed with the finger; the siphon is then put in quickly, and the finger at once washed with water. Sometimes the acid is thus drawn directly into glass carboys, but it is better to employ a series of cooling pots, as shown in figs. 284 & 285. A small portion of the acid is necessarily left in the retorts, and this is useful in refilling them with warm acid of 144° Tw., as it prevents cracking.

In order to prevent the cracking of the retorts by sudden draughts, Jones patented, in 1845, so-called "protectors," consisting of hoods of sheet iron or stoneware, made in two parts, quite covering the neck of the retort. But as this also prevents observation of the liquid, they are inconvenient; and they are quite unnecessary if the house is arranged as described above—that is to say, if it is kept warm, and draughts are excluded by double doors.

The sulphuric-acid vapours formed in the rectifying process in glass retorts should in no case be allowed to get into the chimney. They are partly condensed in the conducting-pipe itself; after issuing from this, they should pass through a small coke condenser, flushed with water, before entering the chimney, to wash out all the acid. The 21st Alkali Report, p. 45, describes the following arrangement:—The necks of the retorts pass into a lead trunk, set on a level, whose bottom is dished with an upstand of three inches, not burnt to the sides. A small stream of water is set running, when the glasses start boiling, at the end of the trunk

nearest the condenser, and the water travels in a contrary direction to the vapours; at the further end it runs out at a lip as acid of 100° Tw. This plan is very effective, and only a small scrubber is required to arrest all the fog of acid vapour escaping from the trunk.

Fehrmann (Fischer's Jahresb. 1886, p. 263) describes the glass concentrating plant at Mülheim on the Rhine. The retorts have a similar shape to those used in England; they are made at Glasgow and cost at Mülheim about 38s. each. There are 32 in a row, holding 6 cwt. each. Each retort is placed in an iron sand-bath to within 4 inches of the neck, and is heated by a separate fire; a 6-inch sheet-iron partition prevents any splashing over from the neighbouring retorts in cases of cracking. Before putting the arm (head) on to the neck of the retort 3 or 4 small leaden washers are put in which prevent the contact between glass and glass. The charging takes place by means of a leaden main, connected with a higher pan, in which chamber-acid is concentrated to 142° Tw.; from this main a thin lead tube branches off in front of each retort, which is lowered for the purpose of charging. The charging takes half an hour for 32 retorts. The emptying is effected by means of glass siphons, set going by an air-pump. The vapours formed during the process are carried away by an 8-inch pipe running along the retorts; this is connected with large lead cylinders, filled with coke and cooled from without, where the distilling acid is condensed, and from these a connection is made to a chimney. All the fireplaces are accessible from the outside of the building; in front of each retort there is a small glass window which allows of observing the boiling, and thereby regulating the fire. It takes 1 or 2 hours before the acid begins to boil, and the whole concentration lasts 8 to 10 hours; the sign of the end is when the acid has been completely decolourized.

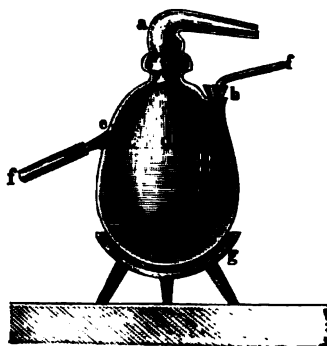
A great improvement on the old plan of intermittent concentration in glass retorts is the *continuously acting plan* of Gridley, patented as a communication by Mr. Henry Chance (No. 1243, 1871). Several retorts are placed terrace-wise in an obliquely ascending furnace and are connected by siphons, so that the top retort is fed by fresh vitriol, which, after being concentrated to some extent, flows into the next lower retort, and so on. The lowest retort is in the hottest part of the furnace. The retorts are shown in detail in fig. 288. *a* is the head, connected with a draught-

pipe common to all the retorts, by which the vapours are conveyed into a small leaden coke-tower and condensed by water. At *b* there is an opening in the shoulder of the retort; into this the funnel passes by which the acid enters the retort; *d* shows the level of the acid; *e* is the tubule attached to the retort, by which the acid leaves it; and *f f* show the glass connectors which convey the acid from one retort to another. The retorts are set in sand in shallow iron pots, *g*. Four beds of retorts, *i. e.* sixteen retorts, will produce, from 6 A.M. on Monday till 12 noon on Saturday, 600 carboys, equal to 46 tons; the labour required consists of two retort-men (day and night turns) and two labourers. The average consumption of coal is 28 lb. per carboy of 175 lb. (=16 per cent.). This process is in very successful operation in most of the vitriol-works in the United States, and has also been largely adopted by manufacturers in England.

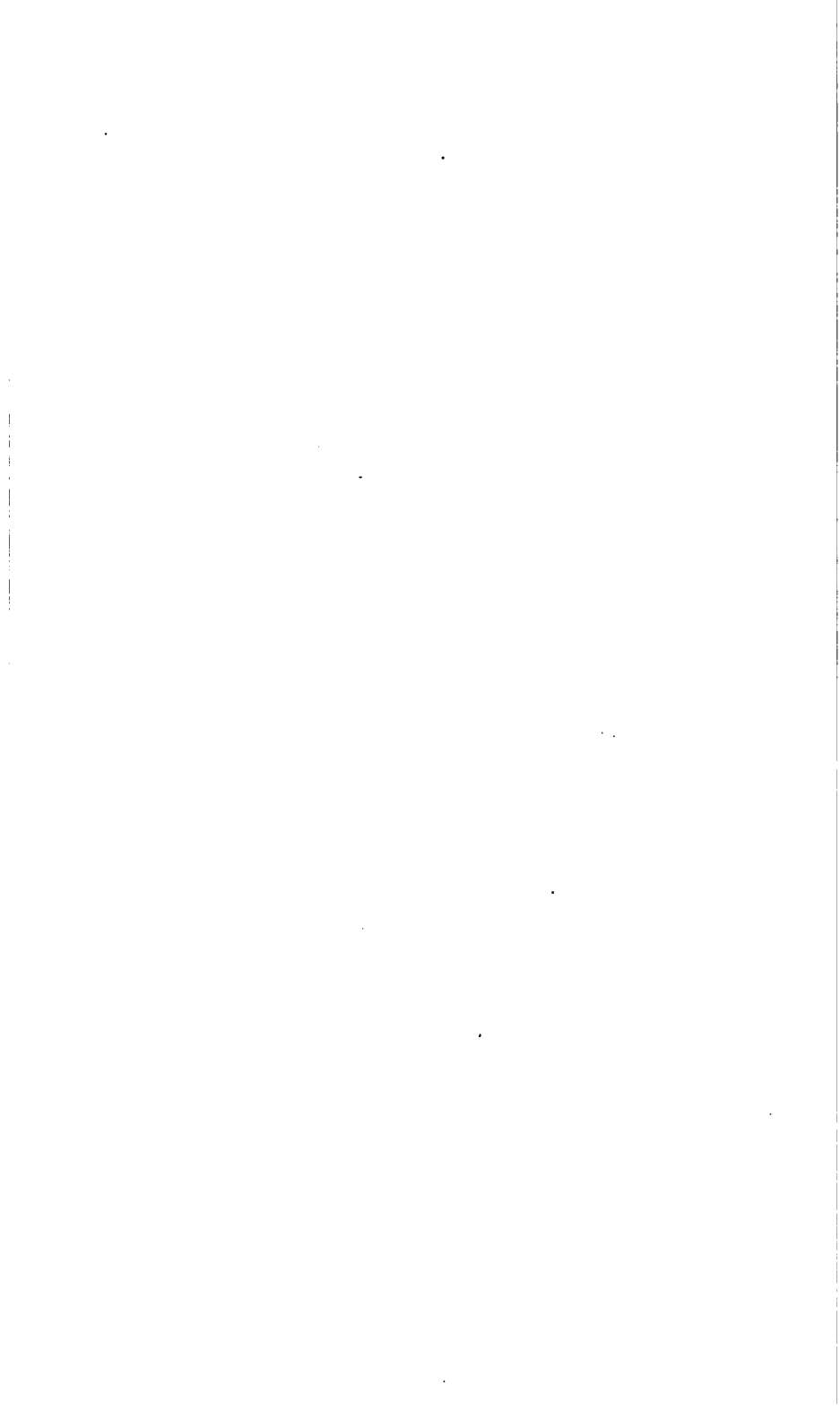
I owe some important communications concerning improvements in the Gridley process to the kindness of Messrs. Chance Brothers, of the Oldbury chemical works, and of their manager, Mr. H. C. D. France. (Part of the following is taken from Dr. Ballard's Report, pp. 173 & 182.) The process has been improved at the above-mentioned works by using ordinary coal-gas as a heating agent, burnt in a Bunsen burner underneath each retort. This has largely increased the output and decreased the labour and breakage. The breakage during a period of two years has only cost 3*d.* per ton. of acid rectified, and the labour has been 1*s.* 10*d.*; but this item could easily be lessened, as the same men could look after plant turning out twice as much. The gas consumed (made at the works themselves), with all leakages and defects, has been 3500 cubic feet per ton of acid of sp. gr. 1·84. (The present consumption of gas is probably even less than that here stated.)

Figs. 289 to 291 show the way in which the four retorts are combined in a set, which are fired from a common gas-pipe.

Fig. 288.







The retorts are first fired till all the acid in each of them has attained full strength; then fresh acid of 144° Tw. is run into the top retort, whereupon the connecting overflow-pipes begin to work and the acid runs from each retort into the next lower one, and from the lowest into a cooler, from which it can be filled into carboys. This process goes on day and night.

A great advantage of the Gridley-Chance plan is this, that it requires no retort-house kept at the temperature of a Turkish bath, like the old plan. It is only necessary to enclose the four retorts themselves in a glass case, similar to the vapour-hoods to be found in every large chemical laboratory, in order to protect the retorts against draughts. The glass case is connected by a pipe with a small leaden coke tower, which communicates with the chimney; any acid vapours escaping from the retorts are condensed here.

The Gridley plant, as arranged at Chance Brothers, is so efficient that with ordinary care breakages of retorts hardly ever occur. But in order to provide against this contingency, the bottom of each fireplace communicates by a pipe with an underground tank; in case of a retort breaking the acid would flow into this tank.

The strength of acid attainable by this (or any similar continuous) process does not exceed 92, or at most 93 per cent., which must not be overlooked in comparing the cost of concentration with different kinds of apparatus.

The cooler for this process is constructed in such a manner that the hot acid first flows through a platinum tube, in which it already loses a good deal of its heat, and then into a leaden box with double walls and external and internal water-cooling. The acid issues perfectly limpid, about 60° C. warm and 168° Tw. strong. (Of course any of the cooling-apparatus connected with platinum stills, as described further on, might be employed here.)

An apparatus altogether similar to Gridley's, in which, however, the glass bottles are replaced by porcelain dishes with glass heads, has been patented by J. Hughes (Amer. Pat. 339,552). Bowen (E. P. 2035, 1883) has patented an apparatus on the same principle, with the addition that the vapours from each lower retort pass into the next higher one, so that very little sulphuric-acid vapour leaves the last retort. [Rational as this seems at the first glance, it is still very doubtful whether in this way the concentration will not be interfered with too much.]

Veitch (E. P. 7901, 1889) employs flat-bottomed retorts, arranged one above another on a stepped terrace within a tapering fire-flue common to them all, the fire being placed at the lowest and widest end, and the flue narrowing upwards. The acid passes in a constant stream, travelling through the whole series. All the retorts can be easily seen.

As to the cost of concentrating in glass, the labour is, of course, greater than in platinum stills, and it is also of a disagreeable kind. The consumption of fuel is sometimes absurdly stated to amount to eight times the consumption with platinum stills; in direct contrast is the following statement by P. W. Hofmann, referring to the cost of concentration at Dienze, where $2\frac{1}{2}$ tons of vitriol are daily made in glass retorts, viz. for 1 ton :—

	<i>s.</i>	<i>d.</i>
4 cwt. of coals	4	0
Wages	3	0
Breakage of carboys	1	0
	<hr/>	
	8	0

If the precaution be taken of replacing all the carboys by new ones after the lapse of six weeks, whether they seem damaged or not, there is next to no breakage of carboys, and the cost of concentration is reduced to 7*s.* 6*d.* per ton (Hofmann's Official Report, 1875, vol. i. p. 188). With this should be compared the very much higher cost for wear and tear of the platinum stills (to be given below), and, on the other hand, the much higher statement by Payen concerning the breakage, which, however, refers to the imperfect retorts of former times. Payen states that at Tennant's works at Glasgow only seven retorts, on an average, break per annum. These retorts are made (by Perceval, Vickers, and Co., of Manchester) from green soda glass, as even in thickness as possible, blown with special care, and cooled very slowly; their weight is about 60 lb. each, and they cost 1*s.* 4*d.* per lb.

Another statement concerning the cost of concentrating in glass retorts is made in the 'Mineral Resources of the United States' for 1886, p. 673, as emanating from a large English works where acid of 60° Baumé, coming from the Glover tower [?], is concentrated to 66° Baumé (8 tons per day) :—

	£	s.	d.
1 ton of coal	0	16	0
Wages and superintendence	2	0	0
Breakage of retorts	0	8	0
Wear and tear of other materials and interest on plant (estimated to cost £200, at 50 per cent. per annum)	0	6	0
Cost of concentrating 8 tons	3	10	0
Cost of concentrating 1 ton	8	9	

[This estimate is evidently utterly unreliable. The amount of coal is absurdly low, the breakage of retorts excessively high. We refrain from quoting the comparative cost of concentration in a Faure and Kessler still given in the same place, as equally misleading.]

The cost of concentrating in a Gridley's apparatus is, of course, considerably lower than in ordinary retorts, as there is less consumption of fuel, less labour, and next to no breakage of retorts.

Concentration in Porcelain Capsules.

Messieurs Ch. Négrier et Cie., at Périgueux, have constructed a furnace for evaporating sulphuric acid from 50° to $65\frac{1}{2}^{\circ}$ B. (say, from 106° to 167° Tw.) in porcelain capsules (E. P. 14022, of 1890). Their apparatus is shown in fig. 292 in section. It consists of two parallel ranges of 8 porcelain capsules, each placed one above the other, so that the acid overflowing from the lip of each upper pan flows into the lower one. The capsules are semicircular, 0.305 metre wide and 0.135 metre deep. Each two dishes placed on the same level are contained in suitable pans, forming cavities of a single cast-iron plate, reaching from one side of the furnace to the other. Asbestos tissue is interposed between the capsules and the metal pans, in order to protect the capsules and prevent burning, which is further lessened by putting fragments of porcelain inside the capsules. In the case of a capsule breaking (which happens but rarely) its contents can escape into the fireplace through several holes left in the metal pans; when this is perceived the feed of acid is stopped, the cover is lifted, and the broken pan is replaced by a fresh one in ten minutes. An iron plate with its two

pans lasts three or four years. They are shaped in such manner that there is no communication between the space below, destined for the fire-gases, and the space above, where the acid vapours are formed, the joints being made good with a cement of asbestos and silicate of soda. When the capsules have been placed in the pans, a layer of coarse sand is put into the space between them up to the edge of the capsules. Each pan has two shoulders destined to prevent the dilatation caused by heat bringing it into contact with the next higher capsule. The brickwork above the level of the capsules is made of silica bricks; the top cover is made of cast-iron or glass. The acid gases are aspirated by a jet of water, or in other suitable manner, and are condensed or not. The heat of the fire-gases issuing from the apparatus is used for bringing up acid from 50° to 60° B. in a similar apparatus or in lead pans.

The figure shows at *a* the feeding-pan, at *b* one of the two parallel lead siphons for feeding, at *c c* one of the two parallel ranges of capsules, *d d* are the double iron pans (0.092 metre deep), *e* fireplace, *f* ash-pit, *g* exit-hole for vapours, *h* cover of iron or glass.

One such apparatus is stated by the inventor to produce from 18 to 20 cwt. concentrated O.V. from acid of 60° B. (142° Tw.), with an expenditure of about 13 per cent. of coals of somewhat inferior quality. According to further information received from the inventors, they bring their acid from 53° to $65^{\circ}\cdot 5$ B. with 21 per cent. of the same coal; the cost of an apparatus is about £20, all told.

The Négrier apparatus takes the dirtiest Glover-tower acid, which cannot be used in glass or platinum retorts, and delivers it quite clear at the bottom, the mud settling down in the dishes. This is a great advantage; but it seems that no great strength of acid can be made, and the plant seems also but little adapted for working on a considerable scale.

In 1890 several French works were mounting this plan experimentally.

Concentration in Platinum Stills.

The arrangement of platinum-stills formerly employed is ver-
fully described and illustrated in the first edition of this work,

pp. 526 to 530. A number of data referring to the sizes, cost, and producing-power of those older stills is also there given; but all this must be considered antiquated, and we shall here describe only the modern shapes of platinum stills.

In consequence of competition with the platinum stills, first by the improved glass retorts, and afterwards by the combined platinum-lead apparatus of Faure and Kessler, the two manufacturers of large platinum apparatus (Desmoutis, Lebrun, & Co., of Paris, and Johnson, Matthey, & Co., of London) both greatly improved the construction of platinum stills. In the first place they made them lighter, by leaving the greatest strength entirely in the bottom, directly exposed to the fire. Already in 1867, Johnson, Matthey, & Co. had exhibited at Paris an apparatus for 5 tons per diem, costing only £1640, and another for 8 tons per diem at £2500. Their apparatus are represented in figs. 293 and 293 *a*. The first shows the flat shape, the second the tall shape of stills; in the latter the head first rises a little to allow the weak acid, condensing at first, to run back again into the still (the dotted lines show the older shape of head, still usual in the French apparatus). With the English construction of the still-head less weak acid is obtained, but less work is done, than with the French

Fig. 293.



Fig. 293 a.

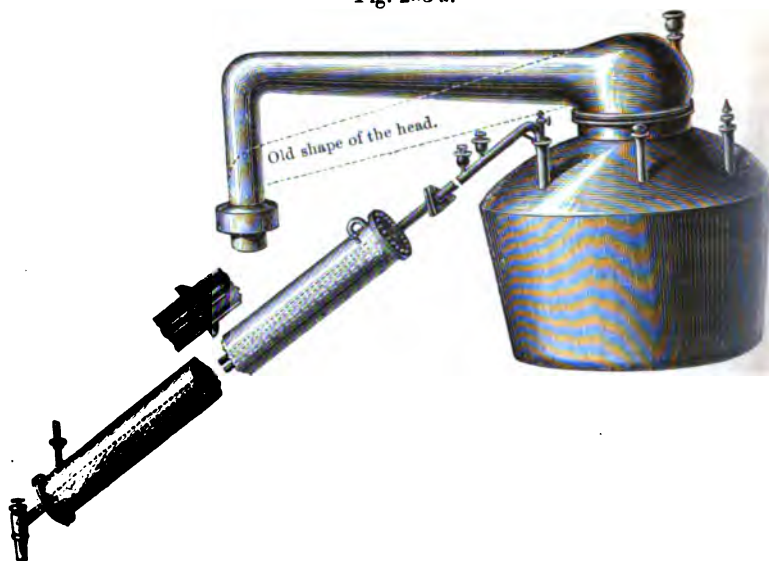
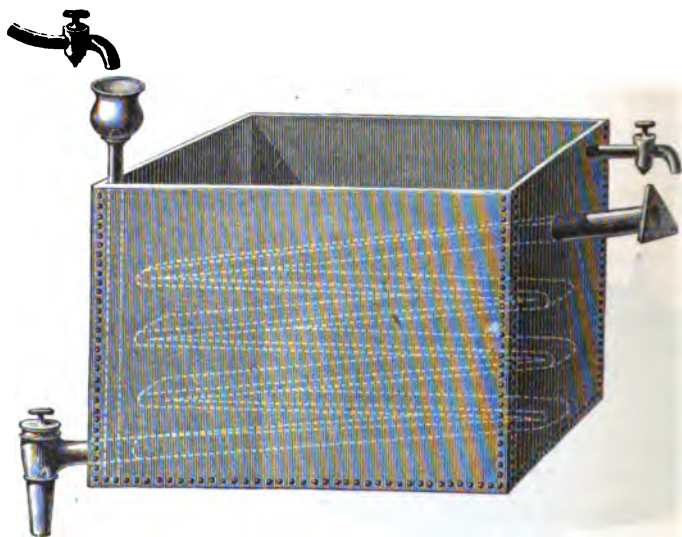


Fig. 294.



apparatus. Fig. 294 shows a cooling-apparatus of peculiar construction, sometimes employed in the English apparatus.

The lightest construction of English platinum stills, where only

the bottom is heated, and which, since 1876, has been most recommended, is shown in fig. 295, along with a new cooling-apparatus. Such a still was exhibited at the London Exhibition of 1862, and since that time has regularly made upwards of 2 tons of vitriol per diem; it originally cost only £675, inclusive of head, tubes, and cooler; and the repairs during 14 years have only amounted to £30. This system is meant for continuous work: when two stills are combined $4\frac{1}{2}$ to 5 tons, with three stills $7\frac{1}{2}$ to 8 tons of vitriol can be produced per diem; but in such cases the cooling-apparatus must be enlarged accordingly. A double apparatus (at original prices) costs £1200, a triple one £1750. A is the platinum still itself, with an ascending head L; it rests on a cast-iron ring C, and is heated by the fire on the grate; below the latter there is an ash-pan filled with water. In the centre of the still-bottom is a funnel D, communicating with the outside by the connecting-tube E; the concentrating acid collects here and is carried away by E. This arrangement is said to have been a great practical success. The tube E is continued into another platinum tube, dipping 2 inches into the funnel of the platinum cooler F. The latter stands in a lead cooler G, which constantly receives fresh water from a tap; the pipe conducting the cooling water to the bottom of G is surrounded by spun yarn or some other bad conductor of heat, so as not to be heated prematurely. From the bottom of F the acid, already cooled to a great extent, runs through an overflow-pipe (likewise wrapped round with spun yarn, to avoid reheating the acid by the hot water in the upper strata) into the stoneware cooler H, which also stands in a cold-water tub. The siphon I, of lead or stoneware, draws the acid from H into the large stoneware bottle K, from which, now sufficiently cooled, it is drawn off by a tap as required.

In the same year (1876) Johnson, Matthey, & Co. introduced a totally different shape of still ("Prentice's system"), in which Faure and Kessler's idea of working with a very thin layer of acid, thereby permitting a diminution of the weight of platinum, was adopted; and it effected at the same time an enlargement of the heating-surface by employing a corrugated still-bottom (Prentice's patent). This apparatus is shown in figs. 296-298. The still B, instead of being round, is of an elongated square or oval shape; for a make of 4 to 5 tons of vitriol per diem it measures 3 feet by 1 foot 6 inches. The acid enters at the back end and comes out

Fig. 295.

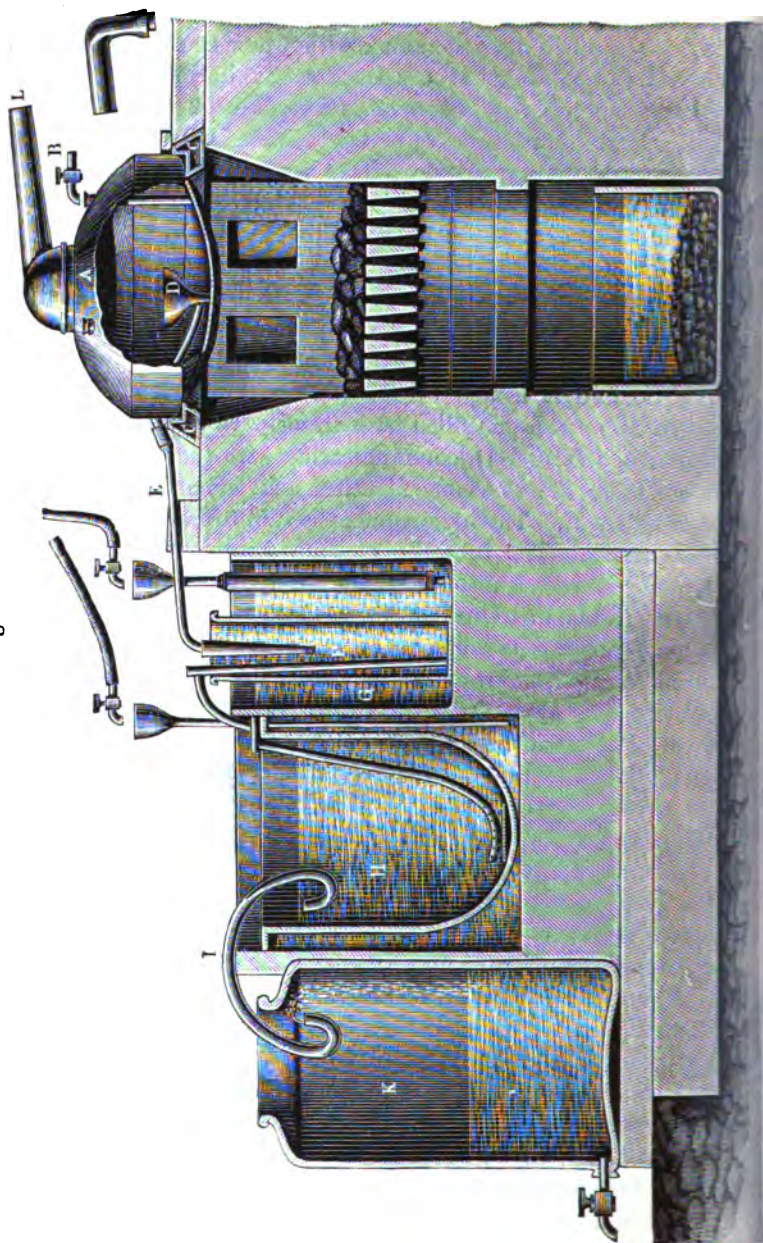
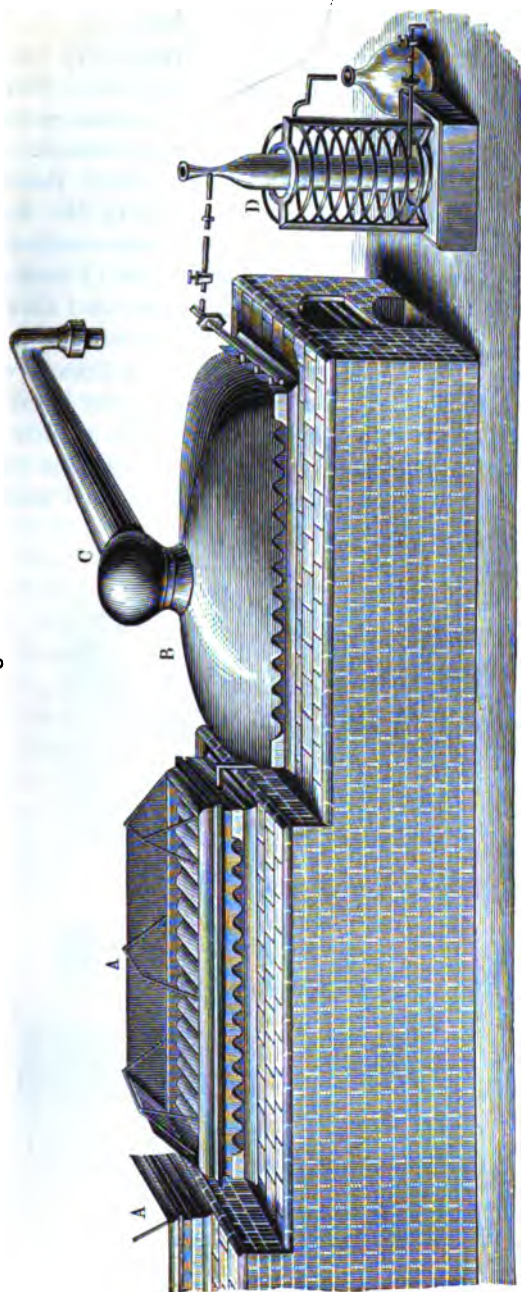


Fig. 298.



in front; the siphon is replaced by an overflow. A still of this kind weighs about $\frac{1}{2}$ cwt., and cost (formerly) about £1000, inclusive of overflow, cooler, metal ring, &c. The firm also supplies platinum pans with corrugated bottoms, as shown at A; but instead of these, ordinary lead pans may be used.

Some further independent statements about these apparatus were made ('Chemische Industrie,' i. p. 194) by Mr. Stroof, of the Griesheim Chemical Works, where three such stills are at work. Each of them consists of a closed still, 2 feet 11 inches by 1 foot $5\frac{1}{2}$ inches, and two open pans, 4 feet 1 inch by 1 foot $5\frac{1}{2}$ inches, and 5 inches deep, the latter with a channel for a water lute running round the upper edge. The pans have a double lead cover with cooling-water; the gas not condensed is taken away by a vertical lead tube into the outer air. The liquids condensing at the sides of this lead roof (water in the first pan, acid of 1.03 sp. gr. in the second) flow into the channel and run away.

Fig. 297.

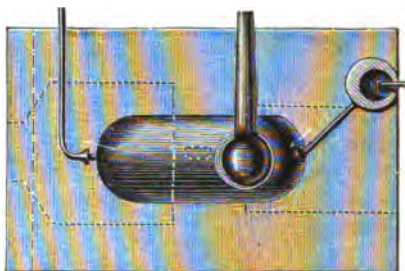
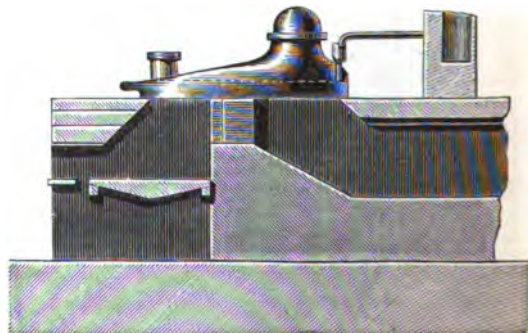


Fig. 298.



Six lead pans, with a heating-surface of 247 square feet, belong to the system. The firing is done by gas-generators. The system concentrates daily 6 tons of vitriol of 1·843 from chamber-acid of 1·55, with a consumption of from 26 to 27 cwt. of Saar coals. The acid in the lead pans reaches a temperature of 125°–135° C. and a strength of 1·68 sp. gr. (measured at 15°), in the first platinum pan 195° and 1·74, in the second 240°–250° and 1·81 sp. gr.; the thermometer under the roof of the first pan shows 90°, under the second 130°. The distillate of the still proper has a specific gravity of 1·45. The still, inclusive of all accessories, weighs 1 qr. 12 lb., each pan 20 to 22 lb. Further statements on the Griesheim stills are found in the 'Chemische Industrie,' 1879, p. 309. The output had risen from 6 tons to 10 tons of strong vitriol per day. As the direct heat applied to the boiler containing the strongest acid damaged the platinum too much, the platinum pan containing the weakest was now put over the fire, which afterwards passed first under the stronger pan, then under the boiler where the final concentration takes place, at last under the six lead pans, which bring the chamber-acid up to about 140° Tw. The platinum is now quite safe; but a saving in coal has not been effected. The leaden cooler for the distilling acid had been replaced with great advantage by a platinum pipe 5 feet long by 2 inches wide [similar to Delplace's, see below]. The vitriol shows on running into the first pan (measured at 15° C.) 134° Tw., into the second pan 155°, into the boiler 165° Tw. The distillate shows from the first pan 0°, from the second 15° to 18°, from the boiler 85° to 90° Tw. The cost of plant for different systems is shown in the following table:—

	Concentrates vitriol per day.	Cost.	Cost per ton of vitriol.	Concentrates for equal cost of plant.
	tons.	£	£	tons.
Old platinum still	7·5	3760	500	38
System of Desmoutis and Co. ...	4·8	1200	250	76
" of Faure and Kessler ...	5·0	1200	240	79
" of Prentice.....	10·0	1890	190	100

The favourable proportion exhibited by Prentice's plan is principally owing to the corrugated bottom of the pans, which increases the heating-surface in the proportion of 1·57 to 1. The thin stratum of acid is a feature common to all more recent plans.

Another system, manufactured by Messrs. Johnson, Matthey, & Co., and introduced at some of the largest works, is that of *Gustave Delplace*, of Namur, which is shown in figs. 299 to 301. In this two stills, A and B, are combined. The top still A is fed with acid of 144° Tw. and the distillate from the still B. The latter, also of platinum, carries on the concentration to the highest attainable point, even up to 98 per cent. H_2SO_4 , if needed.

C C are heads and arms with outlet at D for the strong distillate; the weaker not condensed vapour goes away at E. F is a bottle-shaped cooler for receiving the concentrated acid from the stills. G is a piece attached to the first still for receiving the acid from the lead pans and the distillate from B B. H is a tube for receiving the condensed distillate and carrying it back to A A. In this apparatus the vitriol may be brought to 79 or 80 per cent. SO_3 , or 97 to 98 H_2SO_4 . If this stronger acid, indispensable in the manufacture of dynamite &c., is made, the distillate must be allowed to get up to 150° or 155° Tw., and is always conveyed

Fig. 299.

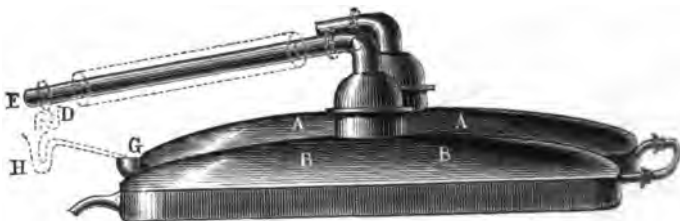


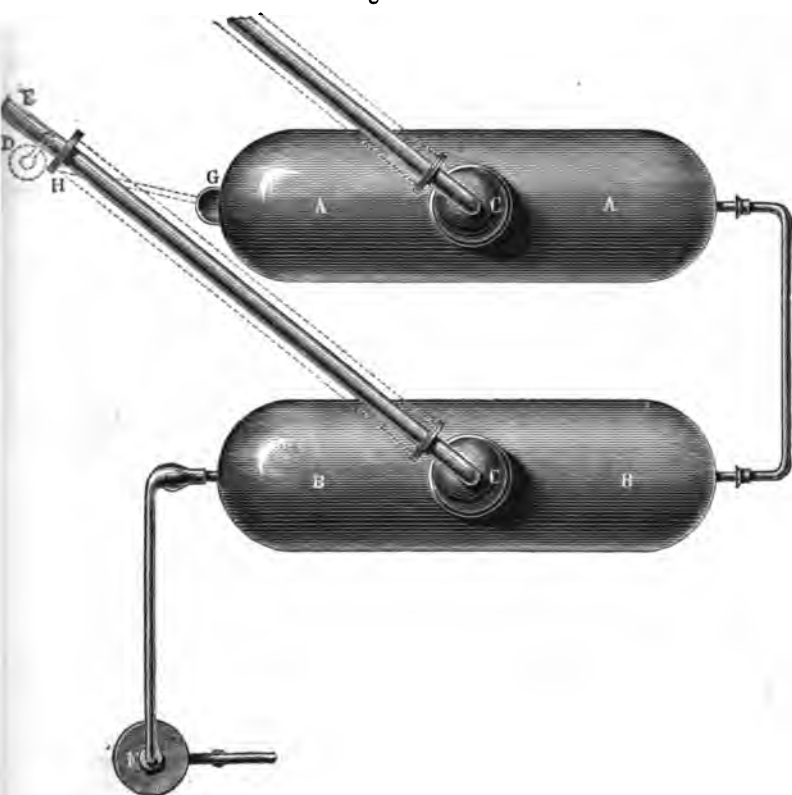
Fig. 300.



back to the first still. For making the ordinary vitriol testing 168° Tw., which really only contains 73 to 76 per cent. SO_3 , the distillate should only show 7° to 23° Tw., according to the speed

of work, the feed-acid being 144° Tw. strong. The following advantage is claimed for the rectangular shape of still—that in working for the most highly concentrated vitriol, the ferric sulphate cannot collect in the opening of the discharging pipe, which generally happens with the ordinary apparatus; the distillate is also said to be weaker, the output larger, in proportion to the evaporating surface, and the consumption of coal smaller than with the round shape. Instead of lead coolers, the distillate is condensed by a platinum tube $2\frac{1}{4}$ inches wide, which is cooled by

Fig. 301.



water for a length of 5 feet; along with the head it weighs no more than the former large head and arm for connection with a lead cooler, without being liable to the frequent need of repairs of

the latter; it also permits condensing vitriol of any strength, free from lead. Consequently the concentration may be carried to any required extent, whilst with lead condensers, and still more with Faure and Kessler's system, the great wear and tear of the lead does not permit this.

For making the very strongest vitriol by a continuous process (which previously was quite impossible), two long stills are preferable to one, the distillate from the second still running back into the first quite hot, without contact with lead; only the first weak distillate escapes. The stills are placed straight over the fire-grate, so that the heat of the fuel is well utilized. The following table gives the strengths of the distillates for concentration to different strengths, assuming the apparatus to be fed with acid of 140° to 144° Tw.:—

Strength of Concentrated Acid. Per cent. SO_3 .	Strength of Distillate. Degr. Tw.
75	15-18
76	23-32
77	51-63
$77\frac{1}{2}$ -78	88-103

When a system of two stills is employed:—

Strength of Concentrated Acid. Per cent. SO_3 .	First Distillate. Degr. Tw.	Second Distillate. Degr. Tw.	Both mixed. Degr. Tw.
75	0-3	15	9
76	3-7	23-31	15-18
78	23-28	75-88	52-64
79-80	41-75	144-150	

The second distillate runs back into the first still.

Amount of work of an apparatus for different strengths of concentrated acid per 24 hours:—

75 per cent. SO_3	12 tons.
76 " "	10 "
77 to 78 " "	8 "
79 to 80 " "	5 "

It is easily seen from the above that concentration up to that point is much more costly than that of less strong acid; but for

some purposes, especially for manufacturing nitroglycerine, the very strongest vitriol is in great request. The value of such acids cannot possibly be estimated by the hydrometer, both because the specific gravities vary too little at that point, and because the iron and lead always present in the acid influence its specific gravity. Recourse must therefore be had to alkalimetical tests.

The cooling of the concentrated acid is done by an upright platinum cylinder standing in water. The acid enters at the top and leaves it at the bottom; the water enters the outer vessel at the bottom and leaves it near the top.

The apparatus is supplied by Messrs. Johnson, Matthey, and Co. by weight, at market prices for platinum. The weight of one boiler is about 50 lb.; head, condenser, and acid-cooler together $17\frac{1}{2}$ lb. With this 5 tons of vitriol of 93 to 94 per cent. monohydrate, or 6 tons of 92 per cent. monohydrate (the common "168° Tw."), are made. A two-boiler apparatus, weighing about 110 lb. with all appurtenances, furnishes 10 tons of vitriol at 93 to 94 per cent. or 12 tons at 92 per cent. in 24 hours. M. Delplace (Ste. Croix 7, Namur) undertakes the erection and starting of the apparatus.

Some improvements have been made in his apparatus by Delplace's patent of 1882 (G. P. 23,159). He provides a long, flat platinum still with an undulated cover, bearing on the top of the four undulations as many still-heads. From that which is nearest to the

Fig. 302.



acid feed, only water distils off; the others yield water with more and more acid, the fourth pretty strong acid. Thus with one pan acid of 98 per cent. H_2SO_4 can be obtained. The bottom is best made in a corrugated shape (as in fig. 296). I am not aware whether this kind of still has been carried out in practice.

The platinum stills built by the Paris firm F. Desmoutis, Lemaire et Cie., as formerly used, before the shallow form had.

been introduced, are shown in the first edition of this work, vol. i. pp. 526 and 536. Since 1876 this form has been replaced by a

Fig. 303.

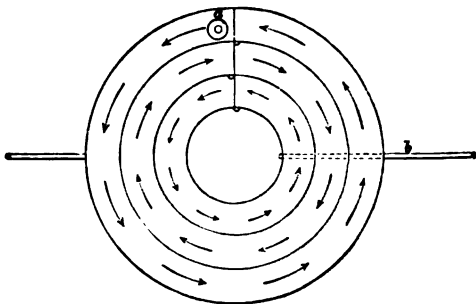


Fig. 304.



shallow still, as shown in fig. 302, and this is frequently made with a bottom fitted with concentric partitions, which force the acid to travel through the still in a circuitous way, as shown by the arrows, and ultimately to flow out through pipe *b*. This is shown in figs. 303 and 304.

(It must not be omitted to note that these partitions are sometimes found to leak, which has caused some manufacturers to abandon this otherwise very rational plan and to return to plain-bottomed stills.)

The latter figure shows a special modification, provided with a removable cover, hydraulically sealed. Figs. 305 and 306 show the setting of these stills, which is extremely simple, the still-bottom resting on a plain cast-iron ring.

Figs. 307 and 308 show a longitudinal still, recently preferred by some French manufacturers, equally provided with partitions.

Fig. 305.

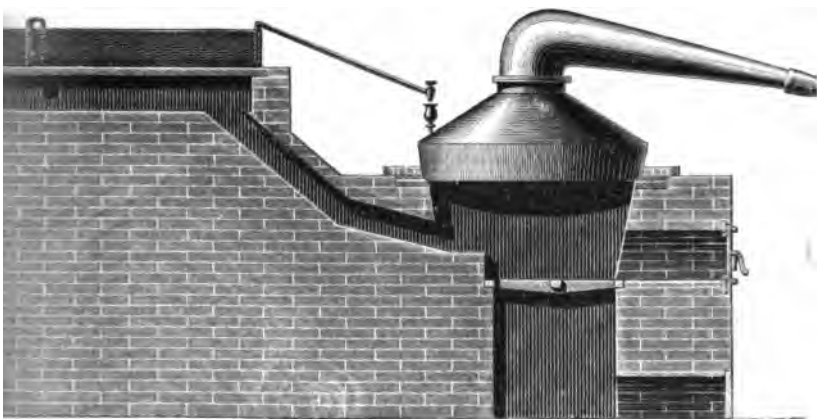


Fig. 306.



Figs. 309 and 310 show the combination of two stills, one of the circular and another of the longitudinal type, which is considered very advantageous for extra highly concentrated acid (see p. 709).

Figs. 311 and 312 show the combination of two longitudinal stills, one of them, A, with partitions like the still in figs. 307 and 308, but with the central portion made of a greater depth (*à gradin*) ; still B has only four cross partitions, dividing the length

into five almost square portions, through which the acid has to make its way gradually, and C is the platinum cooler, of a star-shaped section (not visible in the drawing).

Figs. 307, 308.



The following notes, kindly furnished to me by M. Lemaire, will explain the special advantages attaching to each of these descriptions of stills. Fig. 302 represents the present (1890) type of stills, all made in a piece, for works of middling size, manufacturing commercial acid of $65\frac{1}{2}^{\circ}$ B. Such a still, 0.90 metre in diameter, produces 5 tons concentrated acid in 24 hours; it weighs 22 kilog., the cooler 3 kilog. (if supplied).

The following figures, 303 to 308, show the special type of the Paris firm, viz. the concentric partitions which they consider best adapted for making large quantities of acid containing 93 or 94 per cent. H_2SO_4 . Such a still, weighing 40 to 42 kilog., all com-

plete inclusive of a cooler, produces about 10 tons of concentrated acid with a consumption of coal not exceeding 14 per cent.

Fig. 309.

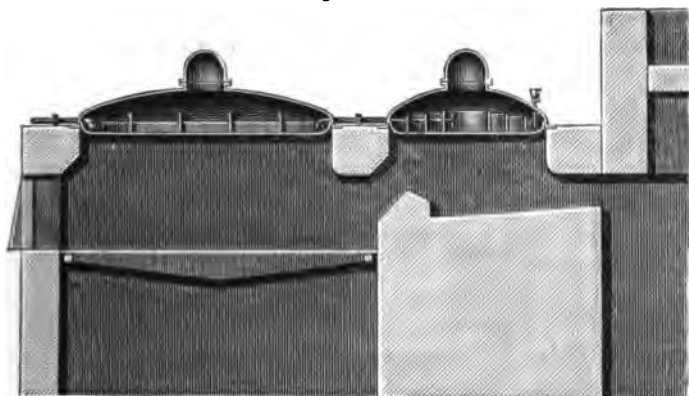
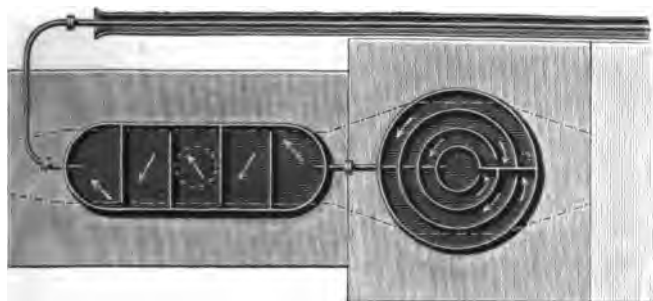


Fig. 310.



Formerly most buyers preferred the circular shape; now some of them prefer the oblong shape as better utilizing the fuel. But common to all are the partitions which cause the acid to flow through the still in a prolonged stream, without any mixture of the concentrated with the dilute acid. This system has now been applied for 15 years with great success. Where two stills are to be worked in combination a difference must be made between the case where acid of $65\frac{1}{2}^{\circ}$ B. and that where acid of 97-98 per cent. is required. In the former case it is best to place both stills on the same fire.

They thus produce slightly less than if fired separately; but this is outweighed by the saving in fuel, labour, and repairs (about 20 per cent. on the fuel and 25 per cent. on labour and repairs). The waste fire-gases cannot concentrate the feeding-acid in the lead pans, which these receive from the chambers, above $59^{\circ}\cdot 5$ B. ($=140^{\circ}$ Tw.); but this is an advantage, as the acid gets less charged with

Fig. 311.

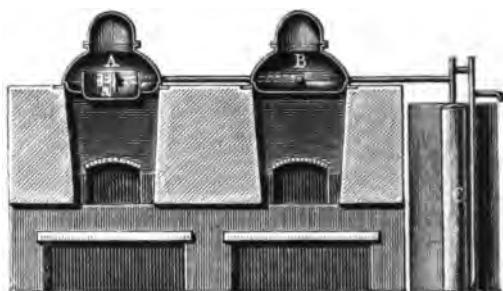
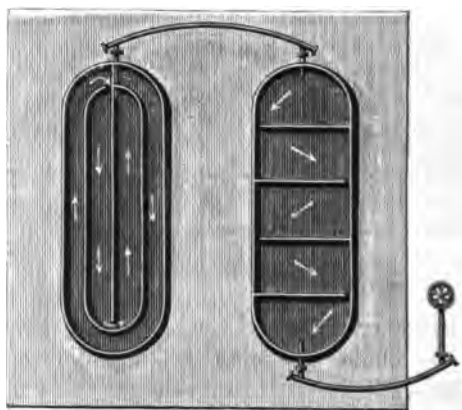


Fig. 312.



lead, and its strength is absolutely regular. The quantity of distilling acid is lessened; the finishing still furnishes a distillate of from 20° to 25° B. ($=32^{\circ}$ to 42° Tw.), whilst the distillate from the first still is almost pure water and is thrown away. This combination is shown in figs. 309 and 310; the two stills, all complete

with a Liebig's cooler, weigh 50 or 51 kilog. for a production of 10 tons in 24 hours.

For concentrating acid up to 97 or 98 per cent. H_2SO_4 two stills must be combined, each of them heated by a separate fire. Figs. 311 and 312 show this system. Whether the stills are circular or oblong, the first (preparatory) still always possesses the above-described concentric partitions, whilst the second (finishing) still has only simple cross partitions, which do not go within more than 1 centimetre ($=\frac{3}{8}$ inch) from the bottom, and thus leave this entirely free. This is done because in this case large quantities of anhydrous ferric sulphate are deposited, which must be constantly removed, so as not to form crusts at the bottom. This cannot be done with concentric partitions, but these can and ought to be employed in the first still, where no such deposit is formed. The two stills, with all accessories, but without cooler, weigh about 60 kilog.; the cooler in this instance is a star-shaped platinum bottle, weighing 4 to 4.5 kilog., and the whole produces and cools 10 tons of acid of 97 per cent.

The first still in fig. 311 shows the "stepped" pattern (modèle à gradin). Here the central compartment is $\frac{3}{4}$ inch deeper than the outer part; this slightly increases the heating-surfaces and slightly shallows the bottom.

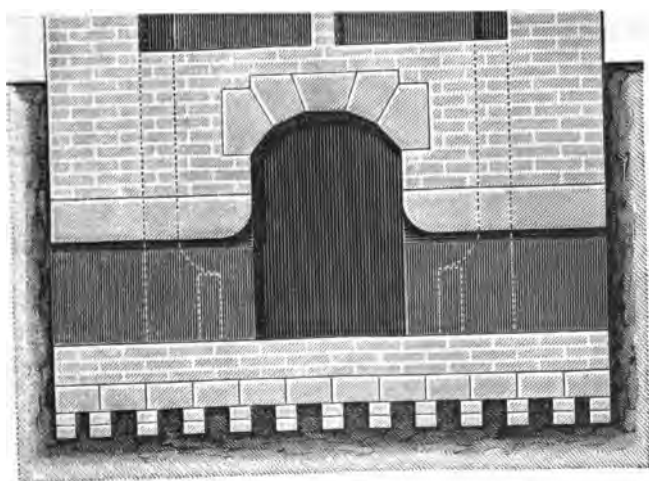
The *art of firing platinum stills* is of the greatest importance, not merely as far as economy of fuel is concerned, but even to a greater extent where it is necessary to manufacture acid of a regular and high degree of concentration. Ordinary hand-fired grates, as shown, for instance, in fig. 295, will do quite well, where the acid need not exceed 95 per cent. H_2SO_4 ; and the waste heat of the flame may be utilized for bringing up the chamber-acid in lead pans to the strength required for feeding the still, say 140° Tw., although in most cases this can be equally effected without any cost by the waste heat of the pyrites burners. But where acid of 96 per cent. is regularly required, it is much better to adopt a plan ensuring perfect regularity of heat; and this becomes indispensable when acid of 97 or 98 per cent. is to be regularly run in a continuous process. This is very easy to understand, for with the very shallow depth of acid now universally employed a slackening of the fire will instantly tell upon the concentration. Supposing the feeding-acid to be of uniform strength (a necessary condition for continuous work), it stands to

reason that the strength of the acid run out in a continuous process must vary with the heat employed, and that, consequently, that heat should also be as uniform as possible. No ordinary fire-grate will fulfil this condition; this may be done by really efficient mechanical stokers; but I am not aware of any case where such have been tried for platinum stills. Another means for attaining the same end is the employment of good gas-producers, and of these the most efficient for the present case seems to be that of Director G. Liegel, of Stralsund (Prussia). A large number of Liegel producers have been already fitted to platinum stills and have been working for many years past; and I am assured on most reliable authority that there is nothing equal to them for obtaining the most highly concentrated acid in a regular way. Figs. 313-318 show the Liegel producer as applied to sulphuric-acid stills; but, of course, special modifications must be made in particular cases, as stated by the inventor of the system.

Concentration in Platinum Dishes with Lead Covers (Faure and Kessler's system).

The first stills constructed on the principle of the platinum bottom-dish, as the only part of the still coming in contact with the hot concentrated acid, with lead covers cooled by water were used by Messrs. Harrison, Blair, and Co., of Bolton, and Mr. A. Smith, of Dublin, some time before 1860, but were given up again. In 1863 M. Kessler proposed his first still, which was erected at Griesheim (Dingl. Journ. vol. clxxvi. pp. 34 & 164; ccxxi. p. 85). This apparatus was not a success, and was replaced 10 years later by the firm of Faure and Kessler, at Clermont-Ferrand, by a new construction which itself has been gradually changed as more experience was gathered. The older forms of the apparatus, which are not used now, are fully described in our first edition pp. 542-551, with many illustrations. We shall here only describe the present form of the apparatus, with the aid of detailed drawings to scale, kindly furnished by the proprietors of the patents, Messieurs F. Desmoutis, Lemaire et Cie., of Paris, platinum works.

Fig. 319 gives a general sketch of the apparatus on a scale of $\frac{1}{2}$.



[To face p. 712.]

Fig. 321.

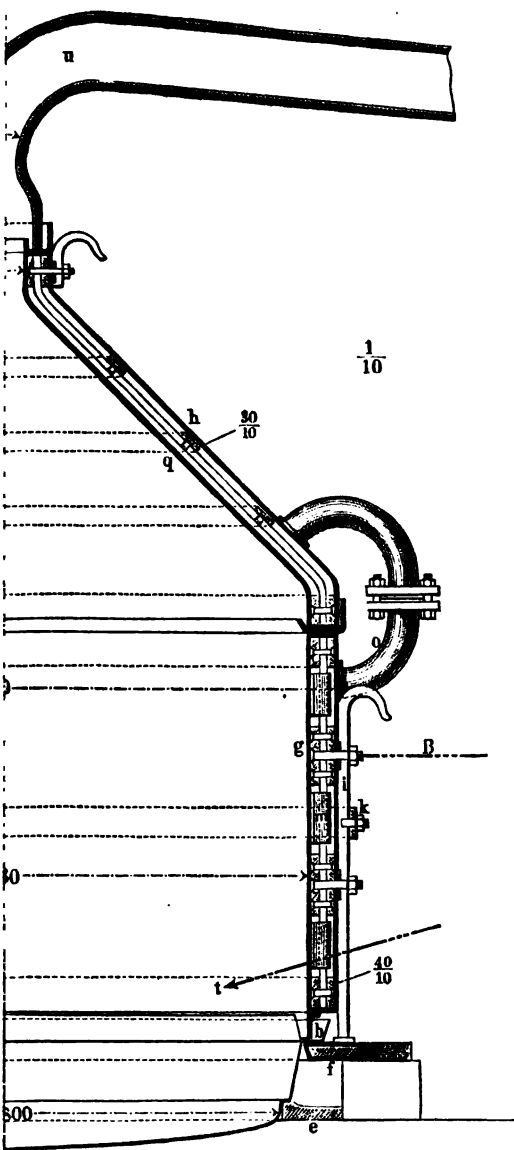
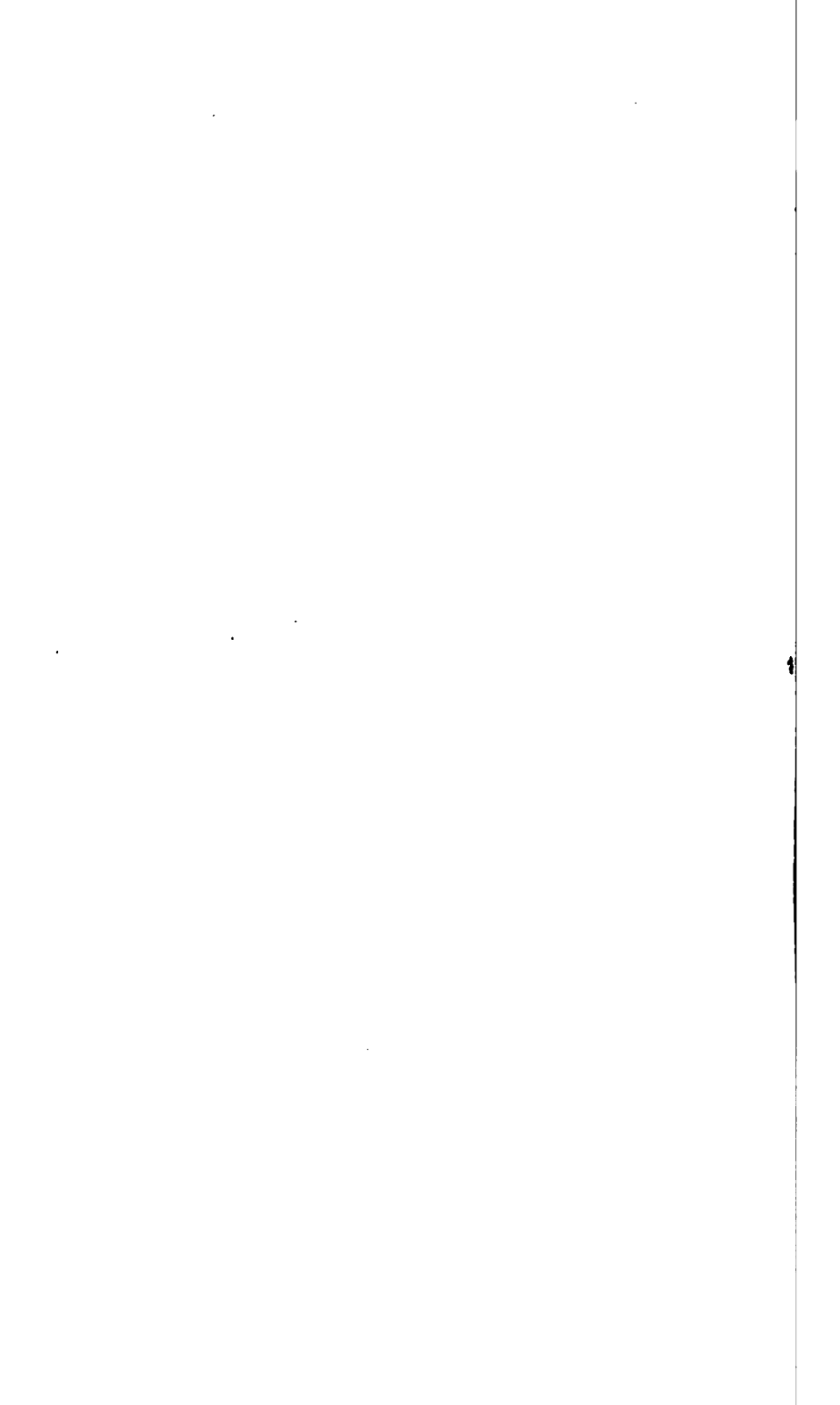


Fig. 320.



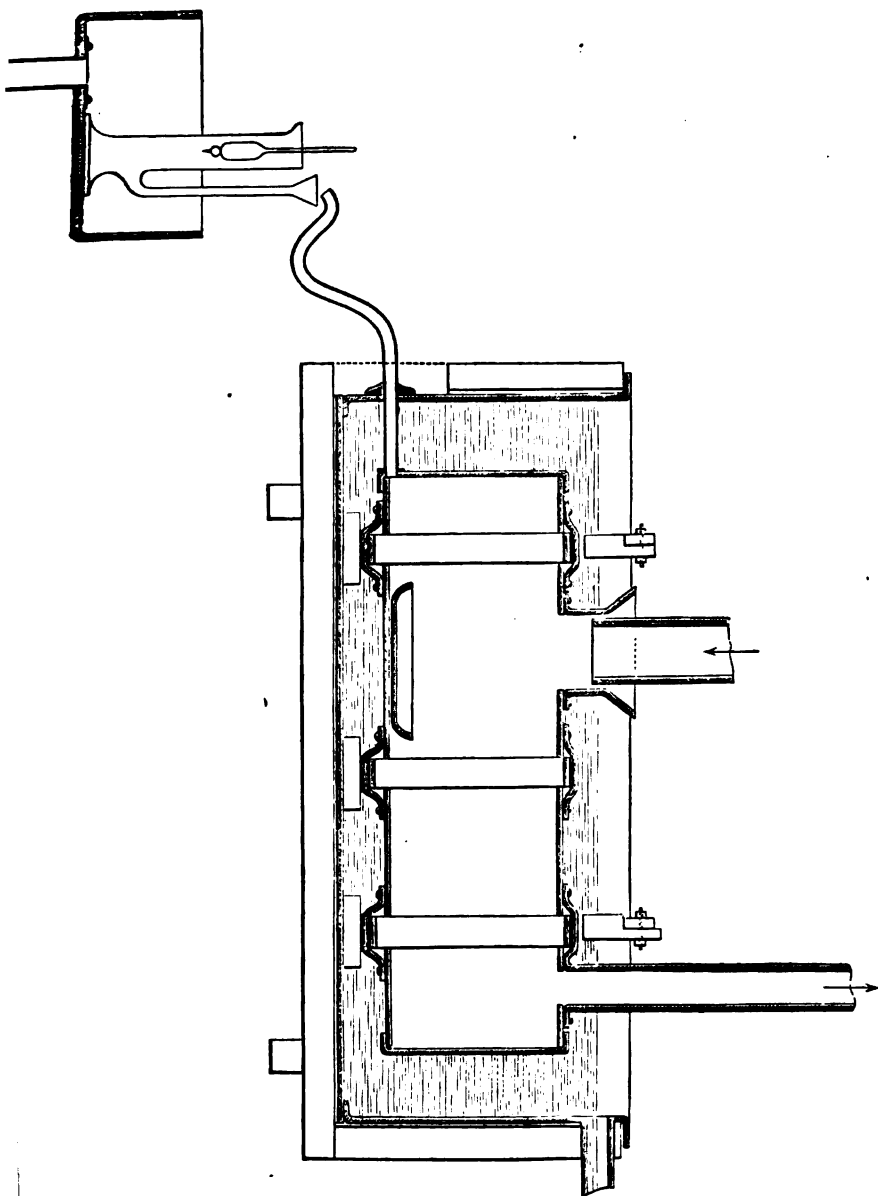
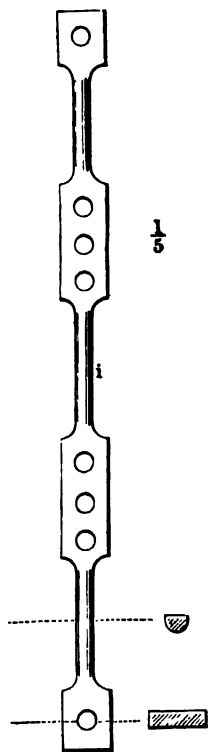


Fig. 320.

a is the platinum basin, with the lead bell *b*, which will be illustrated and described in detail further on. The dilute acid condensing on the sides and top of the bell runs away through pipe *c*. The uncondensed vapours pass away through pipe *d*, which bends downwards and dips into the condenser *e*. The acid formed here, after passing through the hydrometer cylinder *f*, runs away through *g*, together with that from *c*. The cooling-water for the bell enters at *h*, that for the top cover at *i*. The concentrated acid runs away at *k* into the cooler *l*, to be described below, and from this through *m* into carboys, &c.

Fig. 322.



The fire of the fireplace *n* passes either underneath another or even a third platinum basin, each of them placed so much higher than the preceding that the acid can run from one to another, or else directly under a set of lead evaporating-pans, in which chamber-acid of 106° Tw. is brought up to 142°, the proper strength for feeding the platinum basins.

Fig. 320 gives details of the condensing-apparatus for the weak acid, which can be understood without further explanation.

Fig. 321 gives a detailed drawing of the dish and bell, on a scale of $\frac{1}{10}$. *a* is the platinum basin, the size of which must be proportionate to the production intended. In order to stand the work for a considerable time, it should not be too thin; it is necessary to calculate from 2.9 to 3 kilog. of platinum to each ton of 94 per cent. acid made in 24 hours. For instance, a basin capable of turning out 5 tons of strong acid per 24 hours weighs from 14.5 to 15 kilog., and has a diameter of 0.88 metre (= 2 ft. 10 $\frac{3}{4}$ in.); for 7 tons of acid it would weigh 20 or 20.5 kilog., with a diameter of 1.06 metre (= 3 ft. 5 $\frac{1}{2}$ in.); for 1 $\frac{1}{2}$ tons of acid 6.5 kilog., with a diameter of 0.60 metre (= 1 ft. 11 $\frac{3}{4}$ in.).

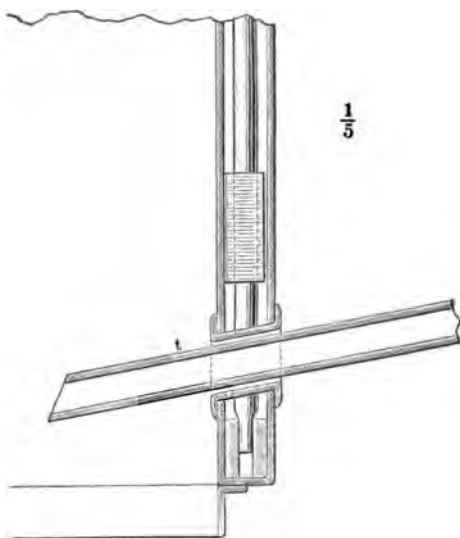
The rim of the basin is shaped like an hydraulic lute, *b b*, with the outlet-tube *c* for the dilute acid condensing on the sides of

the leaden bell, *g g*; this rim is supported by a cast-iron ring, *f*. Further there is an outlet-tube, *d*, for the strong acid, and a supporting ring *e* (of cast-iron) for the lower part of the basin.

The basin is surmounted by a leaden bell, formed of a double-walled cylinder, *g g*, and a double-walled conical hood, *h h*. The cylindrical part is supported on the outside by three iron stanchions, *i i* (comp. also figs. 319 and 321), shown in detail in fig. 322, and an iron hoop, *k k* (40×5 millim.). The pieces *i i* end at the top in hooks, which serve for suspending the bell, *g g*, by means of chains.

The diameter of the cylindrical part is 0.870 metre (=2 ft. $10\frac{1}{4}$ in.) inside and 0.940 (=3 ft. 1 in.) outside. The inner shell has a thickness of 5 millim. (say 11 lb. per superficial foot), the outer 3 millim. (say 7 lb.). Iron rods, *l l*, $\frac{1}{2}$ an inch thick, held

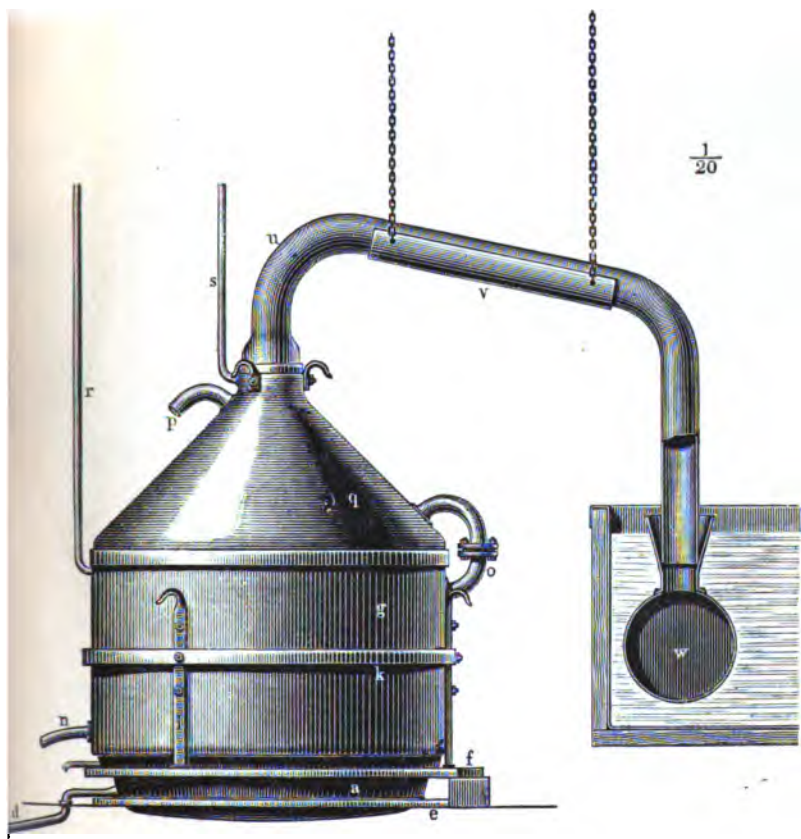
Fig. 323.



by means of straps, *m m*, form a skeleton frame for stiffening the inner cylinders; they are from 3 to 4 inches apart. The pipe *n* serves for introducing cold water in the bottom of the annular space between the two leaden cylinders; pipe *o* conveys the

Fig. 324 gives a horizontal section on the line AB of fig. 321 ;
 g. 325 a front elevation ; fig. 326 shows the iron frame of the
 conical hood *q q*. The letters all have the same signification as in
 g. 319.

Fig. 325.

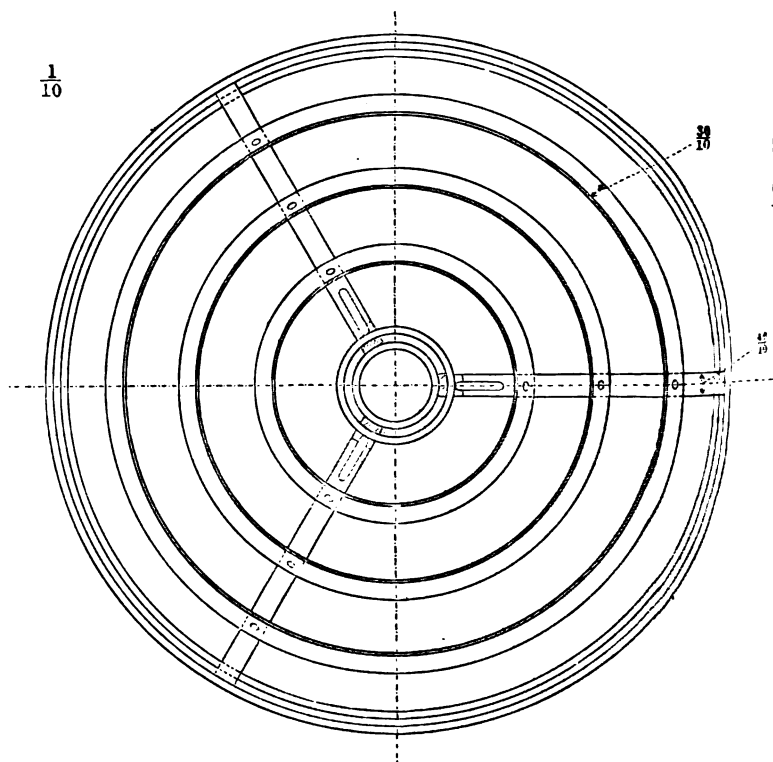


Lastly, fig. 327 gives a perspective view of a set of two Faure and Kessler stills, of a rather older model than that shown in detail above, but capable of giving an idea of the general arrangement.

The cooler employed by Faure and Kessler for the strong vitriol

is made of lead, avoiding the use of platinum, and is shown in fig. 327 *a*. A lead vessel, A, stands on an annular lead cylinder, B, whose base *b* is a little widened out for greater stability. In the middle of the height the partition *c* cuts off the top from the bottom cylinder, the hollow space of A still remaining in communication with the annular space of B. All the hollow spaces are

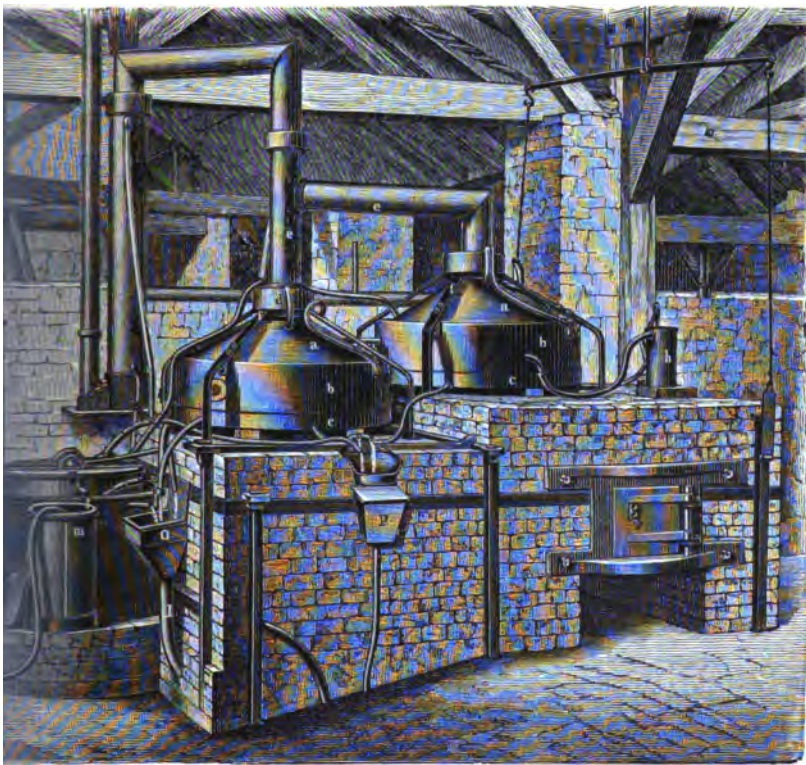
Fig. 326.



filled with vitriol. On the bottom *c* the shallow lead dish *D* is placed; and in its centre the porcelain dish *d* receives the almost boiling acid from the platinum tube *k*, so that the hot acid mixes with cooled acid without injuring the lead at the point of contact. In A there are five worms, *s s*, connected with each other and con-

stantly fed with cold water, which runs off heated at *f*. The whole cooler stands in a cylindrical vessel H, also constantly supplied with cold water through V; the latter, therefore, always fills the inner space *b* of the annular vessel B, circulating through the openings *x x*. Since the acid entering through the tube *t* is much hotter than that

Fig. 327.

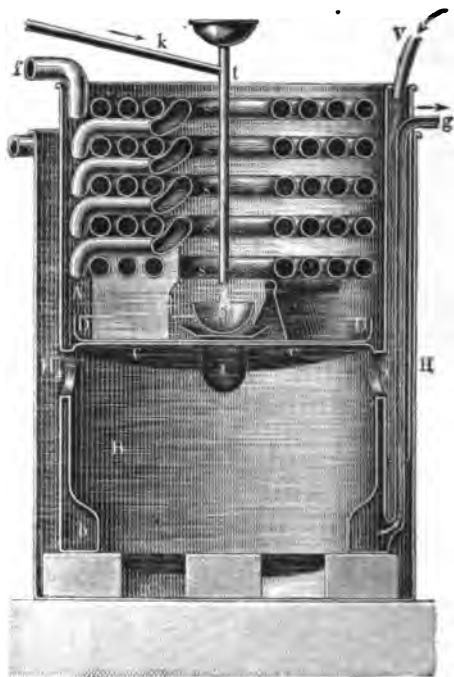


into which it flows, it rises to the top, comes into contact with the worms *s s*, and is partly cooled; it then flows downwards along the sides, and passes into the annular space *b*, where it only forms a thin layer and is further cooled. At last it rises up in the pipe *g*, and from this runs into the carboys. As the diameter of the vessel is about 3 feet 3 inches, the stream of acid moves very slowly

in it, and there is time for cooling. A cooler of the above diameter and equal height suffices for 100 carboys of acid per diem. This apparatus is very ingeniously constructed, but rather complicated. It requires an excellent plumber and incessant cooling with cold water; otherwise it would be very soon destroyed.

The principal feature of the work with the Faure and Kessler stills is this—that the acid, coming hot from the leaden evaporating-pans, is continuously run into the platinum basin, or the

Fig. 327 a.



first of a set of two or three such basins, where it stands in a very shallow layer (two or three inches deep), and is exposed to the direct action of the fire playing upon the whole of the bottom of the dish. This causes such rapid evaporation that the acid, issuing at the side opposite to that from which it had entered, and from the bottom of the still, flows out in a sufficiently concentrated state. The amount of work done is proportionate to the size and

number of the platinum basins. The mixed vapour of acid and water formed in the basins, as it rises up, strikes against the water-cooled sides and top of the leaden hood, and is there condensed to diluted acid, running down the sides and forming a hydraulic lute between them and the platinum dish; an overflow (at c) carries it outside, and prevents it from getting back into the platinum basin. The water-cooling at the same time prevents the leaden hood from damage by the joint action of heat and acid vapours.

The cost of fuel is not perceptibly different with Faure and Kessler stills from that of ordinary platinum stills; and the large quantity of water required for cooling-purposes in the former system is an item of cost to be put against the saving which follows in the cost of plant. It was urged by the inventors as a great advantage of their plan that the loss of platinum was much less than with stills made entirely of platinum; but this is very doubtful, as the wear and tear of the platinum takes place almost entirely in the places which are in contact with the fire-gases, and which are equally large in both systems; and any slight loss of platinum in the other parts of ordinary platinum stills will cost hardly less than the repairs of the very complicated leaden hood and connections of the Faure and Kessler system. According to information from Messrs. Desmoutis, Lemaire et Cie., the bell and hood lasts about two years, and must then be replaced.

I have also obtained the following data from the same firm. The plumbing work for a F. & K. apparatus turning out five tons of acid of 168° Tw. per diem amounts to about 1200 francs, viz.:

For the bell itself	450 francs.
For the acid cooler	350 „
For the vapour condenser ...	250 „
For sundries	150 „
	<hr/>
	1200 „

or about 1 franc per kilog. of the lead employed.

The consumption of cooling-water averages 3 tons per hour, or 75 tons per day.

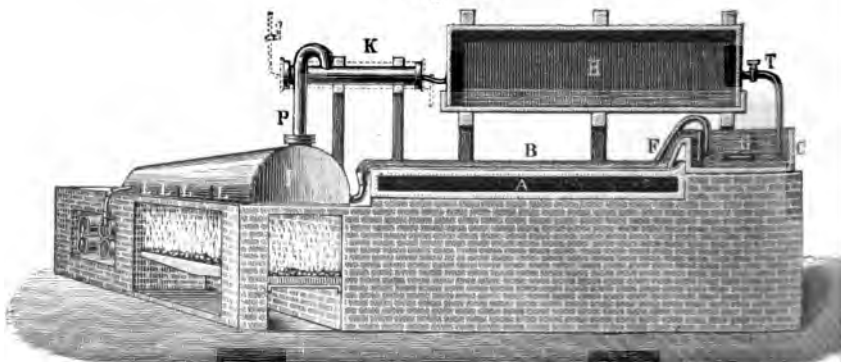
The consumption of fuel is from 18 to 20 per cent. of the acid manufactured.

The great saving in prime cost, and the vigorous advertising of the system, caused a rapid spreading of the Faure and Kessler system, especially in Germany, Austria, and America, much less in France and England. But since the ordinary platinum stills (owing, no doubt, to the stimulus given to the makers by the new system) were considerably improved, and were constructed of much lighter weight and cost for the same output than formerly, and since the drawbacks of frequent repairs, of the great amount of water required, and the frequently minor strength of the acid produced in the Faure and Kessler stills became more perceptible, the latter system has again receded into the background, although, of course, the apparatus once erected are still kept at work. There are probably few new stills put up according to this system, and several manufacturers who had put up this apparatus have replaced it with ordinary stills. The enormously increased price of platinum may give a new impetus to the Faure and Kessler system. It must not be overlooked that the strength really attained by it rarely exceeds 92 or 93 per cent. H_2SO_4 ; but it can be got up to 95 per cent.

Other forms of Platinum Stills.

Bode reports (in Dingl. Journ. cccxxviii. p. 249) on a new platinum apparatus patented in Germany (No. 1005, 9th Oct. 1877) by

Fig. 328.



F. W. Kalbfleisch. The diagram (fig. 328) refers to this. A is a shallow box with bottom and sides of sheet iron, and its top made of steel plate, set in asbestos mortar or some other badly

conducting substance; it carries a shallow lead pan, B, into which the heated acid from C runs through a siphon F. The depth of acid in B is not to be above $\frac{1}{4}$ inch. The heating takes place by superheated steam; thus overheating of the pan by direct exposure to the fire is avoided, and thin sheet lead can be employed. The superfluous steam passes through G, and gives a preliminary heating to the acid in C. The remaining steam may be further used for heating the feed-water of the steam-boilers, and may be ultimately taken through T into the lead chambers. [The various steam-pipes certainly ought to be provided with suitable apparatus for carrying off the condensed steam.] The condenser K is connected with the platinum still I by an upright pipe P; this, as well as the higher situation of the condenser, is much insisted upon by the inventor. The condenser discharges its acid immediately into the lead chamber, H; this, however, is decidedly wrong, as the weak acid will always float at the top, causing the conversion of nitrous acid into nitric acid and quickly corroding the lead. Bode proposes, instead of this, to employ the steam for concentrating the distillate. Behind the platinum vessel the fire is in contact with pipes for overheating the steam, which is to be controlled by a pyrometer.

The platinum vessel is rectangular, with an oval cover, slanting backwards; the reason of this is, because the vessel is fed with acid in front over the outlet-pipe P, and most vapour is given off there. The whole bottom is directly exposed to the fire, and is supported internally by the cross-girders L, soldered to the bottom and the sides and dividing the space into compartments, at the bottom of which the acid communicates and runs off concentrated. The outlet-pipe is bent for a hydraulic lute, the bend determining the level of acid within the vessel; the shallower the acid the more work is done. The acid drawn off is taken from the bottom as usual.

The consumption of fuel is stated at less than half that of the old platinum stills. A vessel of 2 ft. 1 in. \times 4 ft. 2 in. area, costing below £1250 inclusive of cooler, is said to supply 7 tons 6 cwt. of strong vitriol in 24 hours with a consumption of less than 10 cwt. of coals = $6\frac{1}{2}$ per cent.

Bode points out that the platinum vessel is difficult to clean, especially on account of the cross partitions. If the well-known ferric sulphate should be precipitated, weak acid must be sent

through the vessel at a moderate heat; but no control can be exercised. The idea of using the waste heat of the platinum still for super-heating steam seems novel; but the arrangement for utilizing everything to the utmost is extremely complicated, and will hardly stand the test of practice without dropping one thing or the other. The vapours not condensed have been taken into the chamber already by Faure and Kessler; and this Bode prefers to condensing them completely to weak acid, at least when the chamber-gas has no pressure outwards, but suction inwards.

The Kalbfleisch still has been modified by a new patent (Amer. Pat. 267,221; J. Soc. Chem. Ind. 1883, p. 42), which need not be described in detail here. Other American inventions concerning the shape of platinum stills are those of M. Willett (E. P. 9362, 1884) and C. Bartsch (E. P. 6127, 1885). None of these have been, or are likely to be, introduced in European factories, although, for instance, Willett's apparatus is reported to have done well for two years, and to have concentrated the acid [to what point?] with the [almost incredibly] small quantity of 11 per cent. of coal (Chem. Zeit. Report, 1886, p. 16).

Herreshoff, H. Nichols, and G. Nichols (E. P. 1998, 1887) propose making both pure and strong vitriol by the following plan:—The acid, previously concentrated to 86 per cent. H_2SO_4 , is compelled to flow in a zigzag course, being meanwhile exposed to such heat that it is concentrated to 95 or 96 per cent. Thence it flows into another vessel of similar construction, which is heated high enough to drive off $\frac{1}{2}$ to $\frac{2}{3}$ of the acid as vapour, which is collected in a condenser, and will yield acid of 93.5 per cent. and of great purity, whilst the remaining portion contains about 98 per cent. H_2SO_4 .

A platinum dish placed within the gases of a brimstone-burner forms the salient feature of the burner invented by H. Glover, which has been described *supra*, p. 201. In this case the acid is acted upon from all sides, and, in spite of the small size of the platinum dish, a great amount of evaporation is effected, the acid having been previously concentrated up to 140°Tw. in lead pans, receiving the heat of the gases after passing under and over the platinum dish. Glover's platinum dish is rectangular and possesses a double rim, the acid first flowing into the annular space thus

formed, and thence into the interior of the pan. This construction was adopted because it was feared that otherwise the sides of the dish would suffer too much; but it seems unnecessary to take this precaution, and in future the pans are to be made quite plain. The acid stands about 1 inch deep, and is run in and out in a continuous stream. About two thirds of the daily make is here concentrated up to 91 or 92 per cent. H_2SO_4 .

Loss of Platinum.

An important chapter in the concentration of vitriol in platinum is that treating of the *loss of platinum* by gradual solution in sulphuric acid. The first accurate observations on this subject were made by Scheurer-Kestner. He found (Hofmann, 'Report of the Juries, 1862,' p. 16) that, even with perfectly pure sulphuric acid, the loss of platinum amounted to 2 grms. for each ton of vitriol; when nitrogen compounds were present in the acid, it rose to 4 or 5 grms. of platinum: this, however, can be avoided by purification with ammonium sulphate (p. 652). New stills lose less than old ones (about 1 grm.), because newly hammered platinum is more compact and resists the acid better. The iridium-platinum alloy of Desmoutis and Co. (25 to 30 per cent. of iridium) suffers less; in an experiment a dish of pure platinum lost in two months 19.66 per cent., another of iridium-platinum alloy under identical circumstances only 8.88 per cent. of its weight. According to Kerl-Stohmann's 'Chemistry,' vol. iv. p. 1458 (2nd ed.), a small still of that alloy at Halle, of 13 gals. capacity, with a daily output of 12 cwt. of vitriol, stood very well. Heraeus also found that an alloy of 95 platinum + 5 iridium lost only 73 per cent., one of 90 platinum + 10 iridium only 58 per cent. as much as pure platinum. Yet the iridium-platinum alloy has had to be given up, because it is too brittle; pure platinum, from its toughness, malleability, and capacity for welding, is more durable in the long run.

According to more recent statements by Scheurer-Kestner ('Comptes Rendus,' Nov. 1875) the losses of the platinum still at the Thann works were as follows:—During 2 years, a small quantity of nitrogen acids being present, 2.859 grms. for 1000 kilog. strong vitriol of 93 or 94 per cent. SO_4H_2 . In the following year, the nitrogen acids having been removed by ammonium sulphate, 1.220

gram. platinum for 1000 kilog. vitriol. In the following years, when the vitriol contained a little sulphurous acid, the loss of platinum fell to 0.925 gram. Small quantities of hydrochloric acid in the chamber make no difference in the solution of platinum. This, however, is done to a large extent when the strength of the vitriol exceeds the ordinary 66° Baumé of commerce, which contains at most 94 per cent. of SO_4H_2 . The loss in making 180 tons of extra-concentrated vitriol with 97 to 98 per cent. of SO_4H_2 amounted to 6.07–6.65 grms. platinum per ton, in making 102 tons of vitriol of 99½ to 99¾ per cent. of SO_4H_2 , even 8 to 9 grms.; by quantitative analysis 8.38 grms. platinum per ton were actually found.

The above-mentioned experiments refer only to the still itself; but even the accessories are subject to wear and tear, as is shown by the following table:—

	Original weight.	Weight after 5 years' use.
Still.....	30.346	26.450 kilog.
Head	7.255	7.000 „
Siphon	5.689	5.520 „
Small parts.....	1.075	1.000 „
	<hr/>	<hr/>
	44.365	39.970 „
	39.970	
	<hr/>	
Loss	4.395	

Since the still itself had lost only 3.896 kilog. of metal, there was a loss of 12.8 per cent. of the other parts.

This nearly agrees with the statements mentioned by Hasenclever (in Hofmann's 'Report,' 1875, i. p. 188), also originating from Scheurer-Kestner, according to which the loss with ordinary acid amounts to 1.92 gram., with acid containing SO_2 to 1.05 gram., for 1000 kilog.

According to Hasenclever's own experiments (*l. c.*) the loss of platinum at the Hautmont works only amounted to 0.252 gram. per ton of vitriol of 1.8 spec. grav.; if, however, the repairs and the loss in renewing the apparatus are taken into account, the expense amounts to 1.616 franc (= 1s. 3d.) per ton of 1.8 sp. gr. At the Rhenania works the wear and tear of platinum amounts to

5
131
4 30

0.972 grm. of platinum, and the total expenditure for still-repairing to close upon 2s. per ton of 1.8 sp. gr. In both cases the acid was free from nitrogen compounds.

Later on (Compt. Rend. 29th April 1878) Scheurer-Kestner made experiments on the waste of platinum in the preparation of fuming oil of vitriol. The latter was made by heating sodium pyrosulphate in an earthenware retort, lined inside with a sheet of platinum soldered by itself. This weighed 5 kilog.; and after preparing 100 kilog. fuming oil of vitriol it had lost 100 grms.—that is, 1 kilog. platinum per ton of acid. The platinum was found in a soluble form in the residual sulphate of soda. Scheurer-Kestner has moreover established the fact that with the modern platinum apparatus for making ordinary oil of vitriol, whether those of Faure and Kessler, or those of Desmoutis and Co., the quantity of platinum lost is only one fourth of what used to be lost in the former apparatus, viz., only 0.10 grm. per ton for ordinary 170° acid, and from 1.0 to 1.5 grm. per ton for acid of 98–99 per cent. He ascribes this, first, to the much lower boiling-point caused by the little depth of acid, and, secondly, to the much smaller weight of platinum; in Faure and Kessler's apparatus especially a much smaller platinum surface is in contact with the acid than formerly (compare, however, my remarks, p. 721).

In a later communication (Compt. Rend. vol. xc. p. 59) Scheurer-Kestner, in correction of his former statements, points out that platinum is acted upon to any appreciable extent by sulphuric acid only when this contains nitrous acid, but that extraordinarily small quantities of these (0.01 per cent.) suffice for starting such an action, by serving as oxygen carrier from sulphuric acid upon platinum. Therefore even chamber-acid may act upon platinum when containing nitrous acid, which may be the case even in the presence of free SO_2 . Consequently the smell of SO_2 and the pink colour caused by the presence of selenium are no guarantees for the total absence of nitrous acid, whose presence in very small quantities is not detected by ferrous sulphate, but by diphenylamine. If sulphuric acid is freed from nitrous acid by boiling with ammonium sulphate, it has next to no action on platinum, as proved by boiling such acid, or even Nordhausen oil of vitriol with 20 per cent. SO_3 , with platinum.

Messrs. Schnorf, at Uetikon, state the loss of platinum in their Faure-and-Kessler apparatus at 0.75 grm. platinum per ton of

ordinary "rectified" vitriol; for the strongest acid the loss is as much as 10 grms. per ton.

In Knocke's description of the Oker works (Dingl. Journ. cliv. p. 181) it is mentioned that formerly the platinum stills used to be fired with coals, but that wood had been introduced instead, because the still was found damaged in consequence of the sulphur contained in the coals. Even by the formation of carbon-platinum the platinum may become brittle; the fuel, therefore, ought never to come into immediate contact with it.

W. C. Heraeus, in Hanau, found that *gold* resists boiling sulphuric acid much better than platinum. He quotes the following figures, putting the loss of weight of chemically pure platinum = 100 :—

Technically "pure" platinum.....	90
Alloy of 90 platinum + 10 iridium.....	58
Pure gold	13

Which means that pure gold suffers only one-seventh as much as technically pure platinum. At the same time, when 1 kilog. of platinum, worth, say £90, is dissolved, only 144 grams of gold, worth £20, would be lost.

Since pure gold is, of course, too dear for manufacturing stills, Heraeus at his works prepares platinum coated with a firmly adhering layer of gold in the following manner:—An ingot of platinum is brought to a white heat exceeding the melting-point of gold, then a quantity of melted pure gold corresponding to the desired thickness of the coat is poured over it, and the double ingot thus formed is rolled into a sheet. Such sheets are made of the following thicknesses :—

0.4 millim. platinum	0.05 millim. gold.
0.4 " "	0.1 " "
0.3 " "	0.2 " "

Both under the hammer and in the fire these double sheets behave exactly like one metal; they are easily soldered with sheet platinum by means of gold, and are used for the bottoms of the stills, the operation being conducted in such manner that the layer of gold is melted only at the soldering joint. It is not possible to substitute a cheaper metal for platinum, as in this case the slightest injury to the layer of gold would make the apparatus

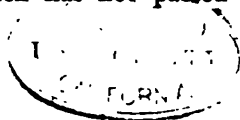
entirely useless, repairs being out of the question. These gold-plated platinum bottoms are especially useful in the manufacture of the strongest (97 to 98 per cent.) oil of vitriol, in which the platinum is strongly acted upon. The proportion of prices (at £90 for platinum, £150 for gold) is as follows:—

Description of Apparatus.	Weight.	Price of platinum entirely.	Price with bottoms		Price with bottoms	
		£	0·4 Pt.	0·1 Au.	0·3 Pt.	0·2 Au.
Delplacestill with concentric undulations 150 × 45 cm.	19 kilog.	1710	1860		2010	
Ditto with parallel undulations 91 × 45 cm. ...	12·5 „	1125	1230		1335	

Several large German works have adopted this system, which is carried out at W. C. Heraeus' platinum-works at Hanau.

Crusts forming in Platinum Stills.

The iron salts contained in the chamber-acid in concentrating are precipitated as anhydrous *ferric sulphate*, which, being insoluble in strong vitriol, partly attaches itself in white crusts to the vessel, partly remains suspended in the acid in shining flakes; the precipitate also contains a little lead. When it occurs in large quantities it may occasion stoppages of work and also make the acid more or less unsaleable. This especially happens when Glover-tower acid is employed for concentration. In order to remedy this, Gerstenhöfer suspended a large porcelain dish in the still by means of platinum wires, completely immersed in the acid, in which, owing to the boiling movement, all crusts &c. collect. It is therefore only necessary to take out the dish from time to time, which can be done very quickly (Bode, Beiträge, 1872, pp. 50, 51). This arrangement seems to have been introduced in very few places, if at all. So much is certain, that hardly anywhere can Glover-tower acid be used for manufacturing "rectified oil of vitriol," and that the acid for this purpose is always obtained by a preliminary concentration of chamber-acid, which has not passed through the



tower, in leaden pans, either by special fires or by steam-coils, or, more often and rationally, by the waste heat of the burner-gas, or by that of the stills themselves, as already frequently mentioned. In any one of these ways the acid is brought up to about 140° Tw. without having been in contact with the flue-dust from the pyrites burners, which contaminates it with a comparatively large quantity of iron.

Even at the works where brimstone is burned the Glover-tower acid has not been found suitable for platinum stills, because it evidently dissolves too much iron (and alumina) from the "packing" of the tower.

But even with feeding-acid concentrated by bottom-heat only, the precipitation of salts in the platinum stills can be very rarely avoided, if the concentration proceeds beyond, say, 92 per cent. H_2SO_4 . Wherever stronger acid is made, it becomes necessary to clean out the platinum stills from time to time, in order to avoid the formation of hard crusts, which would speedily ruin the still. This cleaning is effected by running the still as nearly dry as its form permits, and dissolving the salts by means of hot water or hot weak acid.

This operation has to be performed at various intervals, according to the circumstances of the case. Whilst at some works they have to do it every few days, they may elsewhere run on for several weeks or even months.

An explosion on cleaning out a platinum still has been reported by Kuhlmann, jun. It occurred by running water upon some acid left in the still (the two strata evidently remaining separate) and starting the fire. At a certain point the two strata must have become suddenly mixed; and the explosion occurred through a violent evolution of vapour (Bull. Soc. Chem. vol. xxxiii. p. 50).

Concentration in Iron.

The great cost of platinum, and the liability of glass to breakage, together with the usually great expense for fuel in the latter case, have led to many attempts at employing iron vessels for the concentration of sulphuric acid, as it is well known that iron resists strong acid, although it is so very rapidly dissolved by weaker acid.

It might be thought that *enamelled* cast-iron would be more suitable for this purpose. In fact Roder (Dingl. Journ. cxl.

o. 397) proposed enamelled cast-iron boilers, and indicated a special kind of enamel for them : 1 part of powdered burnt alum, 4 parts of red lead, and 2 parts of pure silica are to be melted together ; the fluxed mass is to be cooled in water, dried, powdered, and 15 parts of it intimately mixed with 20 parts of pure silica and 3 parts of tin oxide. The whole is ground up with spirit of turpentine, laid with a soft hair-brush on the smoothly turned inner surface of the boiler ; and this is repeated three or four times, each coat being allowed to dry first. The enamel is then fixed by fusing on as usual. But even the best enamel will certainly resist only a very short time the boiling vitriol and the uneven expansion and contraction of metal and enamel at the very greatly differing temperatures which occur, and this proposal has had no practical success.

Wolters (G. P. 15,639) states that by heating a mixture of alkaline pyrosulphate with concentrated sulphuric acid in iron vessels a crust of iron sulphide is formed which protects the iron during distillation, so long as the pyrosulphate is left in the vessel.

Seckendorff (Wagner's Jahresb. 1855, p. 56) proposed to concentrate the vitriol in flat-bottomed iron retorts completely surrounded by fire. The retorts are to be filled with lead sulphate, sand, or gypsum ; chamber-acid is to be run in till a paste is formed ; and the retorts are then to be heated. The watery vapour first appearing is conducted into the chambers ; the concentrated vitriol coming after this is to be collected in glass or stoneware vessels, and is said to be very pure, free from iron, and as concentrated as that from platinum ; nor is the iron retort said to be acted upon very strongly. Probably this plan has never been actually tried at all.

A. Nobel, in Paris, proceeds on the following principle (Germ. Patent 10149, 1880) :—Since cast-iron is not acted upon by the vapour of sulphuric acid, the concentrating-apparatus is made in the shape of a column consisting of cast-iron pipes, in which porcelain dishes are placed on ledges. Each dish has an opening, through which a glass rod reaches into the next lower dish ; this is intended to prevent the acid from splashing about in its downflow from dish to dish. When all the dishes are filled, the column is heated by flues surrounding it on the outside. The acid vapour, as well as the concentrated vitriol, is taken away at the bottom. Even nitrous vitriol is said to be used in such towers. [I am not aware whether this plan has been successful.]

J. Grindley (Amer. Pat. 265,495) recommends cast-iron pans, protected at the top by an asbestos cement against the action of the acid. The pan is filled up to the proper level with acid of 66° B., and is fed in such manner that the concentration never sinks below 65° B., in which case the pan is not acted upon. [This strength, equal to less than 90 per cent. H_2SO_4 , is much too low to prevent action on the iron. The corresponding English Patent No. 4709, 1882, has not been proceeded with.]

A new plan was proposed by Hartmann (Patent 2839, 1879). The acid is to be saturated with iron salts, which are again separated on concentration, and are intended to protect the iron of the pan itself.

The following process is intended to combine concentration of sulphuric acid with purification from iron and arsenic. Menzies (E. P. No. 3230, 1883) asserts that sulphuric acid of the highest concentration can contain but traces of iron and arsenic in solution, provided the latter be present as arsenic acid. He adds some nitric acid, in order to oxidize any As_2O_3 to As_2O_5 , and boils the acid in a cast-iron pan, the bottom of which is not exposed to the fire, until the strength of the acid distilling over is about 142° Tw. The fire is now drawn, the acid is allowed to settle, and $\frac{3}{4}$ or $\frac{2}{3}$ of the clear acid is withdrawn. This acid is colourless and free from Fe and As [?], and 3 or 4 per cent. stronger than ordinary "rectified O.V." Fresh oxidized acid is run into that which has remained in the pan, in such a way that the strength never falls below that at which the iron is acted upon by the acid. According to analyses quoted in the 20th Official Alkali Report (for 1883), p. 45, the quantity of iron found in the concentrated acid, calculated as Fe, is only from 0.006 to 0.022 per cent.; that of As, 0.013 to 0.015 per cent.; that of N_2O_5 , 0.011 to 0.024 per cent. The precipitate at the bottom of the still contains 50 SO_3 , 20 As_2O_5 , 28.2 Fe_2O_3 , 1.8 insoluble &c.

These figures show that the removal of arsenic by Menzies's process is nothing like complete. Menzies believes that acid of 58° Baumé does not act (in the heat) upon cast-iron; but that is a great mistake, and in practice he must have dissolved a large quantity of iron which no doubt in the later stage of the process would be again separated in the shape of anhydrous ferric sulphate.

For several years past cast-iron vessels have been in constant use for concentrating sulphuric acid up to the high strength

quired, especially for the manufacture of nitroglycerine and proxyline, say 98 per cent. H_2SO_4 . This strength cannot be attained at all on a manufacturing scale in glass retorts, and in platinum vessels it causes an excessive wear and tear. Moreover the deposits formed in the latter, especially when re-working the spent acid of former operations, are almost unbearable. There is, therefore, a special inducement for employing cast-iron vessels for this purpose, and this is frequently done. The principal condition, which is also (although sometimes to an insufficient extent) mentioned in the above-quoted patents, is this, that cast-iron is not employed below a certain *strength* of acid. It would appear that this strength is really 96 per cent. H_2SO_4 . Up to this point, then, the acid must be brought in glass (which is not easy) or in platinum; but beyond this cast-iron vessels may be employed, if certain precautions are observed. In some places they put in some sulphate of soda, which is believed to preserve the iron. In other places they employ long pans (about 10 feet, and 2 feet deep), covered with a leaden dome, in which the acid (not below 96 per cent.) is heated to 240° . At one end a stream of (heated ?) air is blown in; at the other end the acid vapours escape by a lead tube into a lead condenser. The constant change of air allows of bringing the strength up to 98.5 per cent. At the end of the operation, when drawing off the concentrated acid, enough is left to yield acid of not less than 96 per cent. when feeding with ordinary acid of 93 or 94 per cent. The iron is certainly acted upon, and deposits of anhydrous ferric sulphate are formed; there are also black particles (probably graphite) floating in the liquid. These particles, however, are removed without any special effort by the lead sulphate forming on the leaden cover and falling into the acid, as the sulphate carries down the black particles.

In other places they employ pans with rounded corners, of 6 feet 6 inches by 3 feet 3 inches by 1 foot depth, with a rebate round the top, into which fits a shallow inverted pan provided with three necks (one for feeding, two for the acid vapours). The joints are made good with a mixture of asbestos and silicate of soda solution. Near the bottom there is an outlet-pipe for the acid. The pans are surrounded all over by fire-flues, which keep even the covers hot. Two such pans, placed terrace-wise, and weighing about 10 tons, inclusive of connections, are said to produce (from acid of 42° Tw.) 4 tons of 98 per cent. acid per day, with an expenditure of 25 or 27 per cent. of coals.

The following apparatus serves for the concentration of acid recovered from the "acid-tar" of petroleum refineries. This acid-tar is first diluted with water, whereupon most of the tar is separated and skimmed off. The acid liquor is now concentrated in leaden pans, first by bottom heat and then by top heat, up to a strength of 64° Baumé (American hydrometer). The last concentration takes place in cast-iron pans with leaden hoods. The pans, two of which work together terrace-wise, are 2 × 4 feet wide and 6 inches deep; they have a rim shaped for a hydraulic lute, lined with lead, into which dips a double-walled, roof-shaped, leaden hood, through which water is kept running, on the principle of Faure and Kessler's stills (p. 712 *et seq.*). All the joints are made with asbestos cement. The principle of this apparatus is shown in the sketch, fig. 329.

Fig. 329.



It cannot be denied that under the most favourable circumstances the concentration of sulphuric acid in iron pans is connected with many troubles, and this has led to many firms giving them up again and going in for platinum stills, in spite of their very high price and the great wear and tear when driving the concentration to 98 per cent. acid.

We have previously (*supra*, pp. 140 to 143) discussed the action of sulphuric acid on cast-iron, and we subjoin here further notes on this subject.

Föhr (Fischer's *Jahresb.* 1886, p. 295) points out that iron, in order to resist acids, ought to possess much chemically combined and little graphitoidal carbon, whilst precisely the opposite holds good with reference to resistance against alkali, as in caustic pots and the like. In the former case the iron ought to contain much

manganese and little silicon, in the latter little manganese and much silicon. Fusing alkalies dissolve combined carbon and manganese, but very little graphite or silicon [?]. A mixture which yields good decomposing-pans (or acid concentrating-pans) must yield bad caustic pots, and *vice versa*.

Other Methods for Concentrating Sulphuric Acid.

Stoddart (Chem. News, xxiii. p. 167) has proposed to force a current of air into vitriol heated in a lead pan; acid of 140° Tw. is stated to be obtainable in this way if the temperature be 150° C., and the strongest oil of vitriol at a temperature of 260° C. This plan, if ever carried out on a large scale, was no doubt very soon given up again. There is no reason why a current of air should not do much more harm by cooling the acid than it can do good by carrying away the vapour more quickly, the latter being done much better by top fire, where there is also no danger of splashing. It is well known that lead pans would not very long stand a temperature of 260° C.

Galletly (Chem. News, xxiv. p. 106), who had applied the same principle independently of Stoddart, only worked with a small lead box, 18 inches by 12 inches, in which he obtained from brown vitriol (sp. gr. 1.745) 5 gallons of vitriol of sp. gr. 1.83 by keeping the temperature at 205° C. for one hour, and forcing $16\frac{1}{4}$ cubic feet (roughly measured) of air through the liquid. There was a loss of 11.19 per cent. of acid in this process, as against 8.8 per cent. when using glass retorts. He believed this acid to be recoverable by passing the air into the chambers, forgetting the harm which such a large quantity of air would do there. According to his own admission, a Glasgow manufacturer tried his plan without getting it to succeed.

Gossage (Patent of 1850, Hofmann's 'Report of the Juries,' 1862, p. 17; Muspratt's 'Chemistry,' ii. p. 1047) allows the acid to meet a current of hot air in a chamber filled with pebbles. His apparatus consists of two parts (figs. 330 and 330 a), one of which serves for heating the air, the other for evaporation. The first object is effected by 16 iron tubes, *aa*, open at top and bottom, surrounded by the fire from *b*, which comes to them by the flue *c*. The flame travels downwards in the direction of the arrows, and escapes through *d* into the chimney. The cold air enters the tubes *aa* from below through an arch, *e*, and leaves them at *f*, strongly heated; it passes through *g* and *j* into the concentrating-apparatus.

This consists of two concentric cylinders, *h h*, of $\frac{1}{2}$ -in. lead, leaving a space, *i i*, between them ; at the bottom they are burnt to a lead

Fig. 330.

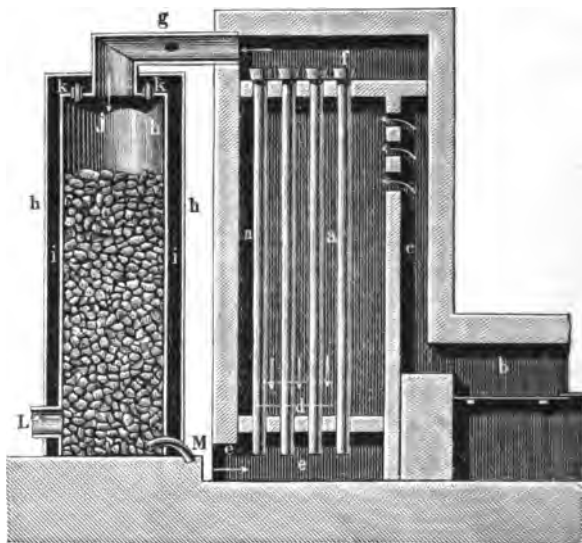


Fig. 330 a.

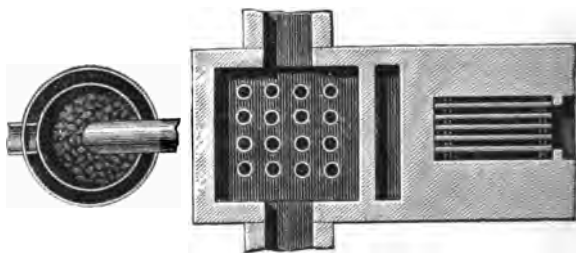


plate. The inner cylinder is closed at the top, except in the centre, where it opens into the pipe *j* ; its inner space is three-fourths filled with pebbles. When the iron tubes have been brought to a red heat, the acid to be concentrated is run on to the cover of the inner cylinder ; it first fills the space between the two cylinders, and then flows through the tubes *k k*, loosely covered by dishes, into the inner cylinder, where it spreads over the pebbles. The hot air entering through *g j*, being in immediate contact with the

vitriol, evaporates the latter quickly, and goes through L into the chimney, charged with steam [and acid vapour]. The acid becomes more and more concentrated as it gets lower down; and with a proper relation between the temperature of the air and the supply of acid, the latter can be drawn off, highly concentrated, by the pipe M. The space *ii* both serves for a preliminary heating of the vitriol and for protecting the lead cylinder. This apparatus has never come into use; its faults are the following:—The air must be made nearly red-hot; and thus the upper lead pipe always melts; the air, charged with vapour, travels in the same direction as the vitriol, and therefore again gives up its water to the latter as it becomes more highly concentrated; all acid escaping along with the hot air is lost in the chimney. Although some of these faults might be avoided by changing the details of construction, the apparatus seems never to have been employed in practical work.

Gossage's plan with heated air has been re-invented by Cotellet, without any additions (Chemical News, xx. p. 107).

S. T. McDougall (Amer. P. 289,293) employs a tower, heated from without, filled with dishes over which the acid flows down whilst heated air ascends in the tower (comp. Nobel's patent, p. 731).

Similar in principle, although very different in detail, is the hot-air concentrator patented by the International Vacuum-Eismaschinen-Verein (G. P. 33,172). It does not seem to have answered, as the same firm a year later took out a patent (No. 38,015) for a totally different apparatus, working with steam, as already mentioned on p. 679.

Finch (E. P. 2207, 1886) combines an evaporating-furnace with two towers filled with refractory material. The furnace-bed is formed by a lead tank, lined with sheet asbestos, and upon this with silica bricks. The roof of the furnace is formed of silica bricks and covered outside with lead. The weak acid first passes through the towers and then into the furnace; the fire-gases make the opposite way. [It is very unlikely that an apparatus such as described will be able to stand the wear and tear of the process for any length of time.]

A very interesting concentrating method, including the use of Field tubes, formed part of an ingenious, but over-complicated

system of the manufacture of sulphuric acid invented by De Hemptinne, of Brussels, and described at length, with diagrams, in our first edition, pp. 507 to 512, to which description we simply refer, as De Hemptinne's process has never been carried out in full and is decidedly impracticable. Another ingenious process of his, described and illustrated in our first edition, pp. 513 to 516, seeks to carry out an idea previously proposed by several other inventors, *e. g.* Kuhlmann (in 1844), viz. concentrating sulphuric acid in a partial vacuum, and thus reducing the temperature to such a point that the whole operation can be carried on in lead. As this process, which was actually at work for some time, has not proved successful, we also refer for it to our first edition. A further modification of his plan has been described by De Hemptinne in the 'Bulletin du Musée de l'Industrie de Belgique,' January 1882.

Monohydrated Sulphuric Acid.

For some purposes sulphuric acid containing no water, or hardly any, and corresponding as nearly as possible to the formula H_2SO_4 , is required. Such acid is extremely useful in certain nitrating and sulphonating operations, connected both with the manufacture of explosives and that of colouring-matters. So great, indeed, has been the want of such a monohydrated acid, that many manufacturers make it from ordinary rectified oil of vitriol and Nordhausen fuming acid, in which case the SO_3 contained in the Nordhausen acid combines with the excess of water existing in the rectified O.V. to form H_2SO_4 . This is, however, a costly process, as is apparent from the following calculations based on Lancashire market prices of 1889, viz.: £2 15s. 6d. for 95 per cent. O.V., and £13 for Nordhausen acid containing 50 per cent. SO_3 . The 5 per cent. of water contained in 95 per cent. O.V. require $\frac{40 \times 5}{9} = 22.2$ parts of SO_3 , or 44.4 parts of 50 per cent. Nordhausen acid, or 8 cwt. 3 qrs. 14 lb. to a ton of rectified O.V.



B, and then again descends into the top of this box. The object of tap E is to shut off the communication between A and B during the time a charge is being blown out of B.

The charging-box B is made of iron and of such a shape that it stretches from side to side right across the tank containing the freezing-cells. It is divided by vertical partitions into the same number of divisions as that of one row of iron freezing-cells G, and each of these divisions is made of such size, that on blowing out its contents it exactly fills one of the cells G to a suitable height. The partitions do not reach quite up to the lid of the charging-box B, so that all the divisions are filled by the supply-pipe C from the store-tank A, and their contents are forced out simultaneously by means of the compressed air, acting through a pipe K, inserted into the lid of the charging-box. Pipe K rises to a higher level than the top of the store-tank A before descending to the air-pump; consequently when A is put into communication with B, the acid fills the entire box B and rises in the air-pipe K up to the level of the store-tank, but it cannot overflow into the air-pump. Pipe K is provided with two taps, of which L communicates with the air-pump, and M with the open air; the latter tap is opened while the box is being charged with acid, and is shut immediately afterwards.

Each of the divisions of box B is provided with a discharge-pipe H, which begins immediately over the curved bottom of the box, passes out of the lid, and rises upwards so far that no acid can overflow during the charging of B from the store-tank A. The discharge-pipes HH then descend side by side, so that the lower end of each is just above one of the freezing-cells G. Thus, as soon as the compressed air begins to act upon the surface of the acid contained in the box, all the discharge-pipes begin to play simultaneously, and all the freezing-cells belonging to that particular row are filled at the same time. When this has been done, a leaden dish J is brought underneath the ends of the pipes, to catch the acid draining out of them and convey it away. The row of freezing-cells, which is suspended in an iron frame N, is moved by means of a travelling crane O to the other end of the freezing-tank F, which contains a number, say 10 or 15, of such rows of freezing-cells. The space between the cells is filled with a solution of calcium chloride, kept a low temperature, say $-20^{\circ}\text{C}.$

or somewhat more or less, by means of any convenient cold-producing machine. Each time a fresh row of cells has been filled, the frames containing the other rows, which rest on pulleys, are moved towards the front end of the tank so as to allow of the last row of cells being lowered into the back part of the freezing-tank.

When the row of cells which has been longest in the freezing-tank has been sufficiently cooled down, it is lifted out by means of the travelling crane O. The cells are then dipped for a few seconds in a vessel containing warm water, in order to detach the frozen mass from the sides of the cell by superficial fusion, and when this has been effected the cells are lifted out and are tilted into a spout or trough P, care being taken to prevent any of the water adhering to the outside of the cell getting into the spout. The spout P contains an Archimedian screw Q, which crushes up the frozen mass and conveys it into a cast-iron centrifugal machine R, placed beside the apparatus. The cells G are then righted again and are ready to receive another charge of rectified oil of vitriol. By the action of the centrifugal machine R, the frozen mass is rapidly separated into a white crystallized mass of monohydrated sulphuric acid and a mother-liquor consisting of less concentrated acid. The latter is either sold in this state (it is equal in strength to good rectified O.V.), or is brought up to full strength by the ordinary processes of concentration. The solid monohydrate is scooped out of R into a pan S, made of iron enamelled inside, and surrounded by a warm-water jacket; here it is melted and is, by means of a tap, run out into carboys or other vessels intended for storing and carrying the product.

Packages for Sulphuric Acid.

Sulphuric acid was formerly always, and is even now to a great extent, sent out in large glass bottles or *carboys* of about 15 gallons capacity, packed in baskets with straw, the projecting necks being still further protected by straw ropes. They are closed by earthenware stoppers dipped in melted brimstone and put in quickly before the sulphur has solidified. Mostly damp clay is put round the top, and a linen rag is tied all over it. Often, especially for short distances, the brimstone is omitted. The baskets only last a short time when exposed to the weather and the damp soil, and especially when any acid gets at them. This

last is sometimes difficult to avoid; after once using, a few drops of acid run down the neck of the carboy and find their way to the bottom of the basket; and the floor of the warehouse, where they are placed, is not easily kept entirely free from acid. Therefore the bottom of the basket is damaged first; and on lifting the carboy the bottle filled with acid forces out the bottom of the basket by its weight and falls through. For this reason a damaged basket ought never to be sent out; some works go upon the principle of *always* packing the returned carboys in fresh baskets. The baskets stand much longer when they are dipped two thirds of their height in coal-tar. In England, baskets made of stout iron wire or of thin hoop iron are now common, protected against quick rusting by a thick coating of coal-tar. In the north of England frequently, sometimes also in Germany, carboy-tubs are used, made of small staves, tapering a little downwards, and bound with iron hoops; the bottle is put in, packed in straw, with only its neck projecting; a circular cover, provided with a hole for the bottle-neck, is put on and fixed. These tub-carboys are rather clumsy and somewhat dearer than basket-carboys, but much more durable; and they afford the great advantage that railways, barges, &c. carry them in two tiers one above the other, which they never do with basket-carboys.

In America, cubical cases are employed, kept together by iron hoops; the bottles are put in with sea-weeds; they cost one third of a dollar per cwt. In France, and also at Aussig in Bohemia, stoneware jars of the size of ordinary glass carboys, and of the same clay as is used for "bombonnes" (acid-receivers), are frequently employed; these can be moved about at the works without baskets, but must be put into baskets for sending out. At Beauvais, where they are made, they cost $1\frac{1}{2}$ franc each.

Sometimes the glass carboys are surrounded with infusorial earth, which in case of breakage absorbs the acid, whilst with straw-packing it runs out and may injure the men or damage railway-trucks. (This way of packing is especially useful in the case of nitric acid, which may cause a fire when coming into contact with straw.)

A special kind of carboy-hampers has been patented by Garneri (E. P. 3190, 1883). "This basket is built up of numerous standard of wood, thin and elastic. The base is preferably com-

posed of two conical and concentric rings, thin, and of 5 to 6 centimetres ($=2$ to $2\frac{3}{8}$ inches) in diameter. The standards are bound and fixed at equal distances between the two conical rings. Wooden rings, placed at intervals in the height of the basket, are fixed both on the exterior and interior by means of a jointed mould, which gives to the basket the desired contour, according to the carboy or other article it is intended to contain."

Schleicher (G. P. 18,112) employs tight-fitting wicker-work baskets, the upper part of which is removable and is connected with the lower part by wire fastenings. This plan is shown in fig. 335. *b* signifies the glass, *e* the joint between the two parts of the wickerwork, *e*₁ the removable part of the latter, *c d* the cover.

Fig. 335.

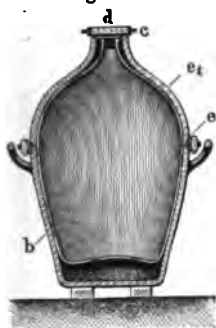


Fig. 336.



The Marple Chemical Company, Marple near Stockport, sells "Carboy Protectors" for the tops of acid-carboys, as shown in fig. 336, which admit of stacking up to four tiers of carboys over one another without any risk of breakage.

Several contrivances have been invented for *emptying acid-carboys*. Some of them consist of iron frames adapted for tilting, others of apparatus adapted to the carboy-necks and acting on the principle of a chemist's wash-bottle, the necessary air-pressure being produced by a small force-pump or by an india-rubber bag with treadle. These and other contrivances are described by Oppler in his report on the Berlin Exhibition of Apparatus for Preventing Accidents (Chem. Ind. 1889, p. 528).

The Aktiengesellschaft für Anilinfabrikation at Berlin has patented (G. P. 8305; Wagner's Jahresb. 1880, p. 236) an apparatus for carrying acid-carboys without in any way putting stress on the handles or other parts of the hampers, so that the carboys

can be safely handled even in rotten hampers. Other contrivances of this kind consist of hand-trucks, on which the carboys are suspended from chains, as shown in fig. 337.

Fig. 337.



Nevertheless, it frequently happens that glass carboys get cracked, either in handling or by the jolting of railway-trucks; and the acid running out is not merely lost, but often does a great deal of damage. The railway and steamboat companies accordingly will only accept acids (vitriol, as well as other mineral acids sent in carboys) at the sender's risk, or else at very high rates for carriage, and only send them by certain trains. Under all circumstances, on account of the bulky nature of this merchandise, a very much higher rate is charged for its conveyance than corresponds to its weight. A truck which carries 10 tons of goods in casks can only carry about $2\frac{1}{2}$ tons of vitriol in carboys. The additional cost of carriage is therefore in direct proportion to the accompanying dead weight and bulk; and as such the water must be regarded which is contained in acid of 141° Tw. (brown vitriol) over and above that in strong vitriol.

The cost of packages also amounts to a good deal. It differs very much, according as the situation is more or less convenient for purchasing the bottles &c.; but it will hardly ever be under £2

per ton of real acid, and is much higher for brown vitriol containing 78 per cent. of SO_4H_2 , than for strong vitriol with 93 per cent. of SO_4H_2 . Of course, the empties are mostly returned; but there is always much breakage, and for longer distances the return-carriage is too dear.

It follows from this that it will only pay for a certain distance, differing very much according to local circumstances, to send out brown vitriol of 144° – 152° Tw. in glass carboys; when the distance exceeds that limit, the extra cost of packages and transit becomes equal to or more than the cost of extra concentration, and the consumers prefer to buy strong vitriol of 168° Tw. Habit, or, more strictly speaking, ignorance, causes some consumers to buy acid of 168° , when 140° or even chamber-acid would do quite well.

For large consumers, and especially for sending great distances by land, glass carboys are not now employed for the carriage of sulphuric acid. For some time leaden or copper vessels were used for this purpose, but these have been abandoned for *wrought-iron vessels*, more especially *tank-waggons*. Balmain and Menzies patented in 1869 this way of carrying sulphuric acid, which, however, seems to have been previously in use locally; its general use seems to date from about 1880. The stronger the acid the less danger is there of any action upon the iron; but even down to 130° Tw. it can be safely carried in iron, provided there are no injurious impurities present, such as nitrous acid, and that the air has no access—the latter, because its moisture condenses on the surface of the acid, forms a layer of dilute acid, and corrodes the iron in that place.

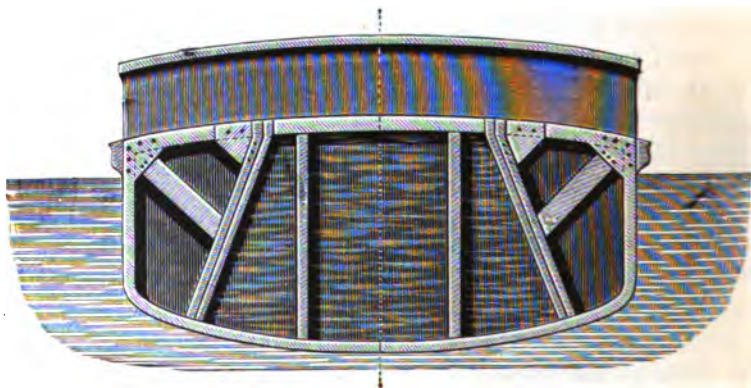
The iron acid-tanks are sometimes made of an angular section, like ordinary railway-trucks; but these have been almost entirely superseded by cylindrical boiler-shaped tanks of 10 tons capacity. A great advantage of the latter is, that they resist pressure, and that, at the consumer's works, they can be fitted with an arrangement for forcing the acid out of them into a store-tank on the premises, so that the tank-waggons are at once emptied and can be sent back to the seller's works. Smaller tanks of this kind, say, holding 2 or $2\frac{1}{2}$ tons, can be used for road-traffic.

In spite of all precautions, a little gas is generally evolved in acid tank-waggons made of iron, which, in opening them, may cause some acid to splash about and injure the men. This is avoided by a contrivance constructed by Vorster and Grüneberg (Oppler, *loc*

citato). On the top of the boiler-tank there is a pipe, and within this another pipe, closed at bottom and open at the top. The annular space thus formed is closed at top and open at bottom. The inner pipe has two lateral openings near its bottom; through these the gas collected in the boiler-tank gets into the inner pipe and thence escapes outside, whilst the acid carried along collects in the annular space between the pipes and runs back again.

Where the acid has to be carried on canals, the boats may be arranged as tanks by lining them with lead (which in such cases is much more suitable than for railway carriage) or even with iron. As was shown by Kuhlmann, jun., in 1878 (*Chem. Ind.* 1879, p. 333) such boats when used for this purpose are subject to dangerous shiftings of the centre of gravity by the oscillations of the acid; but this is entirely prevented by making longitudinal partitions, leaving an air-space widening out at the top, as shown in fig. 338. It is apparent from fig. 339 that the shifting of the centre of gravity is then very slight as compared with the ordinary system (shown in fig. 340).

Fig. 338.



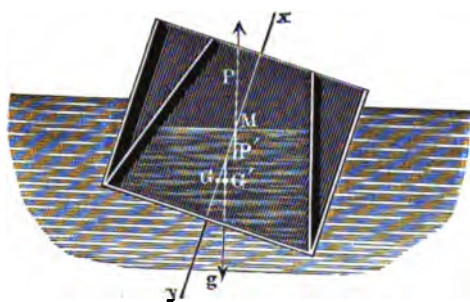
Holden (Patent No. 3805, 1877) proposes to construct acid-tanks from wood which has previously been warmed and soaked with paraffin. The edges are to be made tight by a solution of gutta-percha in naphtha.

For sea transport wooden boxes lined with lead are usually employed; iron would probably answer better.

Vorster and Grüneberg (*G. P.* 24,748) have proposed the

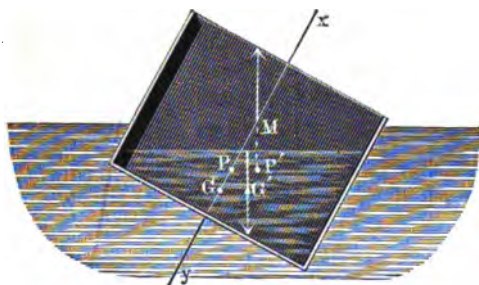
following plan, especially with a view to sea-carriage:—Dry and finely divided *Kieselguhr* (infusorial earth) is saturated with three or four times its weight of strong sulphuric acid. The product, which thus contains at least 75 per cent. of acid, retains its pulverulent form and can be transported by land or sea in lead-coated sheet-iron vessels without any risk of breakage. When it reaches its destination the mass is either used directly or is diluted with water, and the acid is separated from the *Kieselguhr*. This plan has not been found very practical, nor does it seem to be called for, as the pure (liquid) acid itself can be sent out perfectly well in sheet-iron vessels closed by screw-plugs.

Fig. 339.



White and Rickman (E. P. 17,095, 1887) for a similar purpose mix sulphuric acid with anhydrous sodium or magnesium sulphate (hydrochloric acid with calcium or magnesium chloride), dissolving

Fig. 340.



the salt in the acid by the action of heat, and allowing it to solidify on cooling. The salt frequently does not interfere with the use of the acid. This plan is evidently not practical.

CHAPTER XII.

ARRANGEMENT OF THE APPARATUS OF SULPHURIC-ACID WORKS.

ALTHOUGH it is obvious that, no fixed rules can be laid down as to the way in which a sulphuric-acid works should be planned, yet a few remarks upon this subject will not be out of place. In the first place, the arrangement of acid-works depends upon whether they are to supply only chamber-acid or acid up to, at most, 150° Tw., or rectified O.V. The first case, which is that of manure-works, and even of some salt-decomposing works, is, of course, the simplest, no concentrating-apparatus whatever being needed. Formerly such works usually did not possess any, or only small, Gay-Lussac or Glover towers. But although the latter in this case are not called upon to furnish a larger quantity of strong acid than is needed for the Gay-Lussac tower, and as they do furnish much more than that, water has sometimes to be used in order to bring the acid down to the strength required; yet it is most irrational, in view of the waste of water, the yield of acid, and even the nuisance produced by noxious vapours, to work without any or without fully efficient Glover and Gay-Lussac towers.

Where acid concentrated up to 140° or 150° Tw., but of no special degree of purity, is required (that is, generally in works decomposing salt and for a few other purposes), it is easy to obtain the whole of the acid of that strength without any special concentrating-apparatus, by means of Glover towers. Where, however, purer acid has to be made, either for sale or for further concentration in glass or platinum, concentrating-pans must be provided. These may be heated either by the heat of the brimstone or pyrites-burners, and are then of course placed over these, or else over the flue conveying the kiln-gases to the Glover tower; in either case no separate ground-space is required for them.

Or else (which we deem unnecessary in all ordinary cases) they

are heated by special fires, either from the top or from the bottom, or by steam. Most frequently room will be found for this under the acid-chambers or immediately adjoining.

Finally, where rectified oil of vitriol is made, this can be (and in many cases is) done underneath the chambers; but more usually, especially in the case of glass retorts, a special retort-house is constructed for this purpose.

In the following descriptions and diagrams we take no account of the fundamental alterations in the way of conducting the chamber-process as proposed by myself and others (p. 374 *et seq.*), but we adhere to the way of building sulphuric-acid works followed everywhere up to this time. The modifications involved by the adoption of any of the just-mentioned innovations will be easily made by anybody conversant with such matters.

Without taking any further notice of the last concentration of the sulphuric acid, we remark as follows on the arrangement of the remaining apparatus. The lowest level is always occupied by the pyrites- (or brimstone-) burners; only there must be space left for wheeling away the cinders. Accordingly the burners are always erected on the ground-level; and the stone-breakers, if present, are mostly found on the same level. The pyrites in large works arrives on a railway resting on trestles (gears) and is tipped between the trestles, in order to be taken away as it is wanted, to be broken and laid in front of the kilns. Where the supply of ore is quite regular, the stone-breaker can be disposed so that the ore will pass direct from the railway-trucks through the breaker, and arrive broken on the ground-level, thus saving labour. Where the ore is broken by hand, or where it arrives in large and irregular parcels, this cannot be done very well.

Unbroken pyrites, especially non-cupreous, can be stored in the open air without much damage; but after breaking it ought to be protected from the rain. It is sifted directly after; the dust is stored apart from the lumps; and both are taken to the burners across a weighing-machine. The breaking, sifting, and storing of the broken pyrites nearly always takes place underneath the chambers. Where these are high enough above the ground, the burners themselves are also placed beneath them; otherwise they are erected in a separate shed immediately adjoining. Any cooling-pipes or tunnels are arranged along the side or on the top of the chambers. Where the burners are built under the chambers, the outer pillars

of these must be connected by a light open-work wall, to keep the wind off the burners.

The nitre-ovens are nearly always built at the end of each set of burners and as a continuation of it.

The steam-boilers are also sometimes placed under the chambers; it is better to put them in a shed outside, both in order not to injure the timber of the chamber-bottom by steam leaking or blowing out of the safety-valves, and to save the boiler-plate from being corroded by any accidental droppings of acid. In case of an explosion the damage will then not be quite so serious as if the boilers stood directly under the chambers.

As the burners are built on the ground-level, as the chambers are in any case erected at a certain height above it, and as the gas-pipe also enters into the upper part of the chamber, the gas-pipe must necessarily rise a good deal; and the conditions of draught are thus satisfied.

If, however, a Glover tower is to be used, it must be placed between the burners and the chambers. Formerly sometimes a few burners were set aside for working the nitre-ovens by their heat and taking the nitre-gas direct into the first chambers; this is now rarely or ever done, but each set of burners is followed by the nitre-ovens and then by the Glover tower. Where liquid nitric acid is employed, the nitre-oven is simply left out. The Glover tower itself must be placed with its base rather higher than the top of the gas-flue over the burners. In this way the burner-gas can travel horizontally to the tower; but it is generally made to rise a little higher and to descend slightly into the tower, so that any acid splashing into the pipe runs back into the tower. Usually the levels of the Glover tower and the chamber are planned in such a way that the gas issuing from the tower can still enter the chamber below its top. This secures good draught into the chambers, provided there is a sufficiently strong pull at the exit end. Where this is not the case the indispensable draught in the pyrites-burners is sometimes brought about by taking the gas up a high Glover tower, or else upwards from the tower through a special pipe, and then down again through the chamber-top (comp. pp. 428 & 452). The latter plan is illustrated in our present diagrams. In extreme cases injectors or fan-blasts are made to produce the necessary draught (p. 425).

On the other hand, the chambers are sometimes placed so high

that the top of the Glover tower is below their bottom, and the chamber-acid can be run directly into the tower. This is done at a few English and at the Oker works.

The chambers, as mentioned before, are either arranged so that their floors are all at the same level, or so that each following chamber is from 1 to 3 inches higher than the preceding one. A greater difference is not necessary, but is sometimes employed for local reasons. From the last chamber issues a pipe connecting it with the Gay-Lussac tower, which can only exceptionally be placed on a foundation so elevated that this pipe need not descend—certainly a preferable arrangement if the levels permit it. Provision must also be made for interposing a long cooling-channel between the last chamber and the Gay-Lussac tower, unless there is a special small chamber provided for cooling and drying the gas, which chamber receives no steam.

In any case the Gay-Lussac and Glover towers ought to be combined into a set, with the necessary tanks, air-pump, acid-eggs, &c. arranged at the foot, by which the attendance will be much facilitated. In large works with several sets of chambers it is preferred rather to combine several Glover towers, and in any case several Gay-Lussac towers, to form a set.

Although it is of course impossible to lay down a universal plan for building sulphuric-acid works, a generally suitable arrangement is shown in figs. 341 & 342.

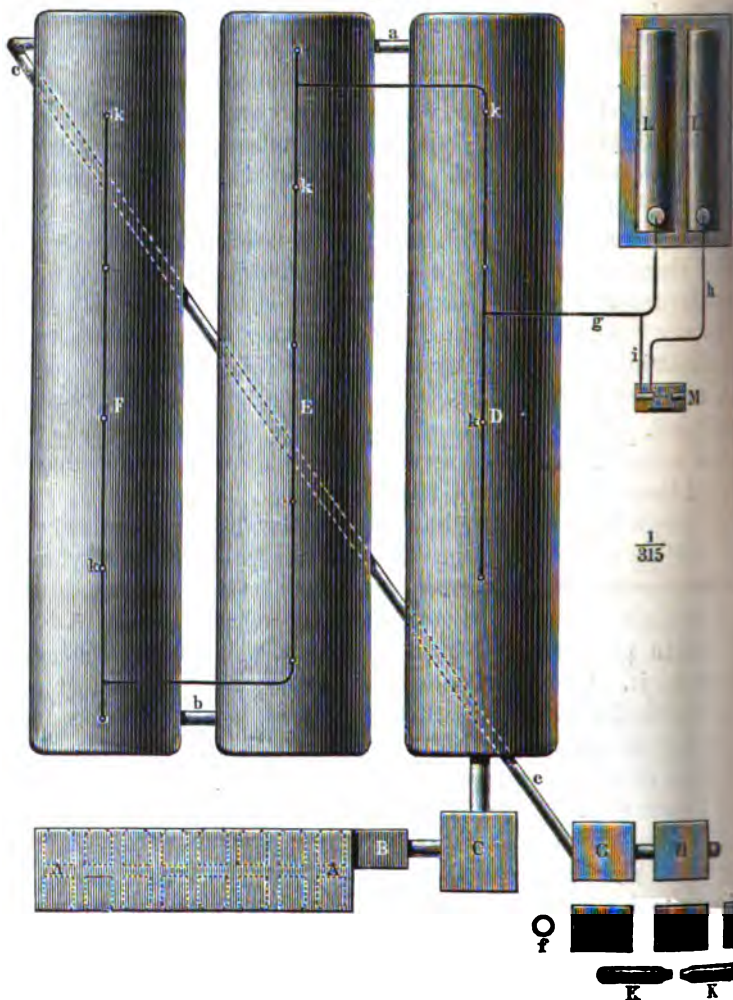
Here no account is taken of the concentration up to 170° Tw. If done in platinum, it takes very little space, and room is easily found for it. The pyrites-burners are not assumed to be placed underneath the chambers; that place will be easily utilized for storing pyrites, coals, carboys, &c., or else, if it is to be used for the kilns or other apparatus, the arrangement can easily be modified to suit this.

The details of the chambers have been purposely shown according to the plan most prevalent on the Continent (the English plan being simpler and easily understood without a special drawing), that is, enclosed in proper buildings, the roof of the chambers being suspended from the frame of the roof of the buildings by iron rods (comp. p. 355), the steam entering in several jets from the top.

The chambers are placed on cast-iron pillars, some of which are utilized for carrying the roof of the building as well. The Gay-Lussac and Glover towers are also put on metal pillars, on which

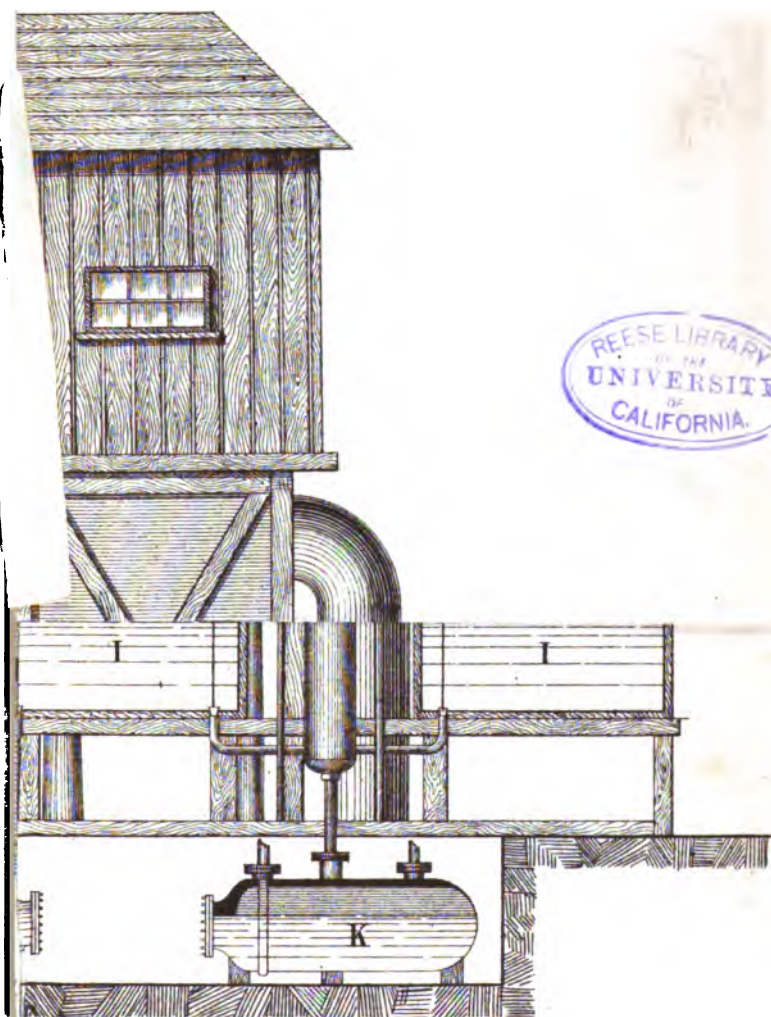
are placed cross-girders and T-irons, the latter forming a continuous support for the lead bottom of the towers. In the case of the Glover tower there is an outer leaden pan, *l*, serving both the

Fig. 342.



purpose of protecting the inner bottom from mechanical wear and tear and cooling the lead and acid by means of the water with which it is filled.

Fig. 341 to face page 752.



30 feet English

JULIUS KLINKHARDT, LEIPZIG.

In fig. 342 we give a block-plan in outline ; in fig. 341 an end elevation on a larger scale, partly as seen from the outside, partly in section. The same letters are used in both figures. A A are the pyrites-burners, which are in this case intended for lumps, in lieu of which, of course, dust-burners may be employed. The burners are built back to back. They are not shown surmounted by evaporating-pans, which will not be necessary where all the acid is used up for manure, for salt-cake, or for sale as brown vitriol ; if purer acid is required, lead pans can be put on as described on p. 670 *et seq.* The burners are followed by the nitre-oven B, which, of course, is unnecessary where nitric acid is supplied in the liquid form. Then follows the Glover tower C, of which the lower half is packed with bricks, the upper half with stoneware dishes or cylinders. The gas now enters into the first chamber D, and then travels on to the second chamber E and the third chamber F. The connections are shown at *a* and *b*. From the last chamber the gas goes on by the long pipe *cc* (in which we notice the "sight" *d*) to the two Gay-Lussac towers G and H, and ultimately through pipe *e* to the main flue leading to the chimney. I, I, I are tanks for chamber-acid, nitrous vitriol, and Glover-tower acid ; K, K, acid-eggs ; *f* is the cooling-arrangement for the Glover-tower acid ; L L' are the steam boilers for supplying the chambers and the air-pump M ; as shown here, boiler L works at low pressure and sends the steam through pipe *g* directly into the chambers, whilst boiler L' works at higher pressure and supplies the steam for the air-pump M through pipe *h* ; the exhaust steam going away through *i* enters pipe *g*, and is thus utilized for the chambers as well. The steam is distributed over the chambers by the cocks *k, k*.

Most of the details shown in fig. 341 explain themselves ; we need only add the following observations. The diagram is made to scale (1 : 63), and may serve as a model for real constructions, only some of the small details (thicknesses of metals, &c.) being necessarily on an exaggerated scale. The arrangement is made in such manner that the steam-boilers, Glover and Gay-Lussac towers, acid-tanks, &c. are placed on one side, so that a second set of chambers and burners may be put up on the other side (to the right side of the plan), utilizing the same boilers, acid-tanks, acid-eggs, &c., and placing the towers in one line with those of the first set, which greatly facilitates the supervision and economizes labour.

CHAPTER XIII.

YIELDS AND COSTS OF SULPHURIC-ACID MANUFACTURE.

IN calculating the cost of manufacturing sulphuric acid, we must take into account the following factors :—

- Cost of sulphur (brimstone or pyrites);
- Consumption of nitrate;
- Consumption of fuel;
- Wages;
- Wear and tear of apparatus;
- Interest on capital, general expenses, &c.;
- Yield of sulphuric acid.

We will in the first place inquire into the *consumption of nitre* and the *yield*. We are here met at the outset by the difficulty of comparing the statements from different sources, arising from different fundamental quantities being taken as the basis of the calculation. Some calculate all the sulphur contained in the charge, others only that portion which has actually been burnt, not taking into account the sulphur left in the cinders. The latter way of calculating is more rational in theory; but in practice it is often less useful than the former. For it is known with perfect accuracy how much pyrites and how much sulphur contained in it has been put into the burners; but as the percentage of sulphur in the cinders varies, it is not known precisely how much has been burnt. Besides, the question is not only how the chamber process itself works, but also how the burning has been done, on which the smaller or larger residue of sulphur in the cinders depends. It is different when the percentage of sulphur in the cinders is almost constant and altogether very slight, as it

burning pure ores in shelf-burners; in this case it is indifferent which way of stating the results is adopted.

The *consumption of nitre* is stated sometimes in percentages of pure sodium nitrate, sometimes in percentages of commercial nitrate; and in the latter case either 95, 96, or 97 per cent. is assumed. Here also we have a source of uncertainty and divergence, although not of such importance as that just mentioned. To each part of sodium nitrate correspond 63.53 parts of N_2O_5 or 74.12 parts of NO_3H or 134.76 of nitric acid of 1.34 sp. gr. (at $15^\circ C.$), the strength usually employed in vitriol-works.

The worst confusion prevails regarding the calculation of the *yield of sulphuric acid*. Some state it in terms of chamber-acid of 50° Baumé ($=106^\circ$ Tw.), some as 60° Baumé ($=144^\circ$ Tw.), some as commercial 168° Tw. ($=66^\circ$ Baumé), some as real monohydrate; what is worse, the reduction upon these terms is made by very varying and, in part, quite erroneous tables (comp. p. 118); and frequently it is quite uncertain whether by "oil of vitriol" (O. V.) an acid of 93 to 94, or one of 96 to 98, or one of 100 per cent. SO_4H_2 is meant. In the following, so far as the sources permit, all statements will be reduced to the only rational term, that of monohydrate, SO_4H_2 .

Frequently, at works where none of the sulphuric acid is sold, but the whole is used for making salt-cake, the yield is calculated indirectly, from the quantity of common salt decomposed by it, according to more or less arbitrary assumptions regarding the quantity of sulphuric acid consumed for decomposing a unit of salt. Thus several large manufacturers, working with open roasters, assume a consumption (and consequently a make) of 81.33 parts of SO_4H_2 to each 100 parts of common salt. Now, in muffle furnaces (blind roasters) decidedly less vitriol is consumed than in open roasters; and yet a large Alsatian maker, using blind roasters only, assumes a consumption of 74 per cent. of vitriol of 66° Baumé on the sulphate, $=85.8$ per cent. on the salt, or 80.8 per cent. of real SO_4H_2 on the salt, which is all but equal to the above-named figure. This proves the uncertainty of such bases of calculation.

Consistently, several English alkali-works have latterly given up calculating the yield of sulphuric acid altogether; they only state the yield of salt-cake upon the pyrites burnt, or upon the sulphur contained therein. Of course, this way of calculating is only pos-

sible where no acid is sold or used for any other purpose than decomposing salt.

Often no mention is made whether that portion of the sulphuric acid employed for the *decomposition of nitre*, which leaves the factory in the shape of acid sulphate, has been allowed for in the calculation. We do this in the following, wherever it can be done from the sources.

Of course the following enumeration does not contain all and every statement of the kind scattered in innumerable publications, but only so much as suffices for forming a good idea of the state of matters.

I. CONSUMPTION OF NITRE.

(Compare also the statements concerning some English works, p. 373.)

1. For Brimstone Acid.

(a) *Without Recovery of the Nitre-gas.*

To 100 parts of brimstone charged:—6 to 9 parts (Knapp, *Chem. Technologie*, 1866, i. pp. 2, 298); at least 6, sometimes $7\frac{1}{2}$ parts (Schwarzenberg, *l. c.* p. 400); 6 to 8 parts (Payen, *Précis*, 1877, i. p. 322); 7 to 8 parts (Scheurer-Kestner, in *Wurtz's Dict. de Chim.* iii. p. 158); 8·9 parts (Stevenson and Williamson, in *Richardson and Watts's Chem. Technol.* iii. p. 318); 10 parts (Wright, *Chem. News*, xvi. p. 93). Most of the sulphur-burning works enumerated in the Official Alkali Report for 1885 consumed 9 or 10 parts.

(b) *Recovering the Nitre-gas.*

4 to 5 parts (Knapp, *l. c.*); 3 parts (Schwarzenberg, *l. c.* p. 401); 5 parts (Payen, p. 322); 3 to 4 parts (Scheurer-Kestner, *l. c.*); 3 parts (several American works visited by myself in 1890).

2. For Pyrites-acid.

(a) *Without Recovery of Nitre.*

At the Oker works in 1857, 14·4 parts; 1859 to 1863, 13·4 to 300 parts strong vitriol (Knapp, *Kerl-Stohmann*); to 100 sulphur charged in the shape of pyrites, 10 parts (Schwarzenberg, *l. c.*

p. 432), 9 to 11 parts (Payen), 12 to 14 parts (Scheurer-Kestner). According to Wright (*l. c.*), in different works, with pyrites of 45 to 50 per cent. 8·5 parts, of 30 to 50 per cent. 10 to 12 parts, of 35 per cent. 12·5 parts; with a set of chambers in bad repair, in the first year 9·31, in the second 9·84, in the third 10·02 parts. According to Gossage (*ap.* Richardson and Watts, p. 317) 13·3 parts with 30 per cent. Irish pyrites. From my own experience, on an average, with pyrites of 40 to 44 per cent. 10·8 parts; in neighbouring works 10·5 parts with smalls, 9·4 with lumps. At some French works I was informed of a consumption of 1·5 to 1·97 kilog. nitre per 100 kilog. acid of 50° Baumé, equivalent to 2·9 to 3·8 kilog. per 100 kilog. pyrites of 44·4 per cent., or 6·5 to 8·5 kilog. per 100 kilog. of the sulphur contained therein. [This statement appears not trustworthy, viz. too low, looking at the figures from the same source for working with a Gay-Lussac tower.] Naville's statements see below.

(b) *Recovering the Nitre-gas.*

To 100 sulphur in the pyrites :—5 parts (Schwarzenberg, p. 432); 7 parts (Payen, p. 322); 7 to 8 parts, less with higher towers (Scheurer-Kestner, *l. c.*); 3·8 parts (Glover). According to my own experience (with insufficient absorbing-space) 3·5 to 4·5 parts; but when the work was irregular, chambers out of repair, as much as 6 or even 7 parts. Neighbouring large works 3·5 parts. K. Walter guarantees 0·7 part of nitre to 100 parts acid of 66° Baumé=2·04 parts to 100 sulphur in 44-per-cent. pyrites. At the Oker works (Bräuning) 3·75 to 4·5 parts per 100 sulphur were used with pyrites pretty rich in sulphur, 4·5 to 6 parts with mixed and galeniferous ores. In French works (same source as above), per 100 kilog. acid of 50° Baumé 0·9 to 1·24 kilog., per 100 pyrites 1·73 to 2·38, per 100 sulphur charged 3·85 to 5·37 parts of nitre. According to notes collected by myself in 1878:—in German works, 2·3 to 3·1 nitre per 100 sulphur; in the best English works, about 3 per cent. (exceptionally, as stated by Affleck, 2·2 per cent.; in Lancashire some large works use even 5 per cent., comp. the Table in the sixth Chapter, p. 373); in French works, (with a Glover tower) 2·7 parts, (without) 4·2 to 4·7 parts to 100 sulphur charged.

In winter there is always less nitre used than in summer. As

between nitric acid and solid nitre no difference worth mentioning can be established; if any thing, slightly less nitre is used in the solid form than as nitric acid, if not the acid itself, but the nitre from which it was originally made is taken as the basis of calculation, as it ought to be.

Notes collected during the last few years:—English works 2·5 to 3·5 per cent. At one works they asserted that the actual loss was only 15 lb. nitre per ton of pyrites, that is, less than 1·5 per cent. on the sulphur, with only 17 cub. ft. chamber-space, and a yield of $41\frac{1}{2}$ cwt., 96 per cent. salt-cake.

A first-class German works with specially good absorbing-apparatus and 16 cub. ft. chamber-space:—1·8 to 2·2 per cent. NaNO_3 on sulphur burnt.

II. YIELD OF SULPHURIC ACID (SO_4H_2).

(Theoretically 306·25 parts per 100 sulphur.)

1st. *From brimstone* (always upon the sulphur actually burnt). 290 to 300, on the average 296 (Knapp); $297 \text{ SO}_4\text{H}_2 = 319\cdot35$ acid of 66° Baumé (Schwarzenberg); “usually 296 to 300; even the theoretical quantity has been obtained” (sic! Payen, i. p. 321); 290 to 300 (Scheurer-Kestner). At some American works visited by myself in 1890, the yield of acid was stated = 305 real H_2SO_4 , which must be an error, attributable to wrong specific-gravity tables, &c.

2nd. *From pyrites*. At Oker, in 1857, 1 cwt. acid of 66° Baumé per 1·89 cwt. ore (Knapp); 1859–63, per 1·729 cwt. ore (Kerl-Stohmann); 1877, in the same place, 160 chamber-acid of 50° Baumé (106° Tw.) were obtained from 100 pyrites; from 100 rich copper-ores 140 to 150 parts of chamber-acid, from 100 “mixed ores” 90, from 100 ore mixed with galena 70 parts of chamber-acid. The residual sulphur in the cinders from pyrites (always containing galena) amounts to 6 per cent., from the other ores to 10–12 per cent. (Bräuning).

In four Belgian works, 1854 (Official Report), on 100 parts sulphur in the pyrites charged 242, 237, 259, 238 parts SO_4H_2 . The same works in 1874 by improved arrangement had arrived at 87·81, 92·17, 85·50, 89·30 per cent. of the theoretical quantity, or 268·8, 282·4, 261·8, 273·5 SO_4H_2 per 100 S (Chandelon).

In the best French works (Schwarzenberg), on 100 sulphur in

the pyrites charged, 259·7 SO_4H_2 ; on the sulphur really burnt, 283·43. Payen (p. 322) makes precisely the same statement, with the addition that *usually* from 100 kilog. 46-per-cent. pyrites 100 to 115 kilog. acid are obtained ($=239\cdot1$ to $250\ \text{SO}_4\text{H}_2$ per 100 sulphur). According to Scheurer-Kestner (*l. c.*) there ought to be the same yield on the really burnt sulphur of pyrites as upon brimstone, viz. 290 to 300 parts. According to Wright, with rich Spanish pyrites 82 to 84 per cent. of the sulphur is obtained as acid; of the loss of 16 to 18 per cent. 4 or 5 per cent. is sulphur left in the cinders, and 12 or 13 per cent. other losses. This means a yield of 251 to $257\cdot25\ \text{SO}_4\text{H}_2$ per 100 sulphur charged (evidently with insufficient chamber-space). An anonymous chemist (in the Chem. News, xiv. p. 22) states the yield from 30-per-cent. Irish pyrites $=82$ to $81\cdot1$ per cent. of the theoretical, inclusive of the sulphur in the cinders.

My own experience and reliable statements personally obtained by me from large factories (where, however, the acid made was mostly calculated from the salt decomposed) are as follows:—
 (a) 238·5 SO_4H_2 on the sulphur charged, with 40-per-cent. small pyrites burnt in muffle furnaces; (b) 240 SO_4H_2 , ditto, with 42-per-cent. lump ore: both without a Gay-Lussac tower. (c) 263·2 on sulphur charged (own experience), with Gay-Lussac tower, but the work being several times interrupted. (d) 272 to 275 ditto (own experience), with a Glover and a Gay-Lussac tower, the latter not large enough. (e) 276·4 on the sulphur charged, or 301·5 on the sulphur burnt (average result of a large, well-managed factory with Glover and Gay-Lussac towers). (f) a number of notes collected in 1878 from the best German and French works agree remarkably closely to a yield of 270–272 SO_4H_2 on the sulphur charged, or 285 to 290 on sulphur burnt. In the warmer climates the yield, even with sufficient chamber-space, is always found somewhat less in summer than in winter, about 3 per cent.

The consumption of coals for chamber-steam is stated $=16\cdot8$ kilog. per 100 kilog. SO_4H_2 as the average of eight French factories working without Glover towers; at an English works with Glover tower the coal used for the chambers and the air-pump amounted to 17·5 parts per 100 parts of SO_4H_2 . Other statements, partly above, partly below those just mentioned, will be found in the following calculations.

Naville (Lunge & Naville, 'Fabrication de la Soude,' i. p. 413) gives the following statements from French works, for periods before 1880 :—

	Expended for 100 parts of H_2SO_4 produced.				H_2SO_4 produced :	
	Pyrites:		Nitro: parts.	Coals: parts.	for each 100 parts sulphur: parts.	per cubic metre in 24 hours.
	parts.	per cent. S.				
a.....	73	49.5	1.45	19.0	277	about 1.5
b.....	88.50	42.3	2.70	12.2	267	1.58
c.....	92	41	3.14	13	265.2	2.10
d.....	95.2	40	2.96	12	262.4	1.60
e.....	100	40	3.10	12	250	1.58
f.....	93	40	2.75	11-12	268.5	1.28

a. Shelf-burner, Gay-Lussac and Glover towers.

b. Oliver-Perret furnaces, no Gay-Lussac or Glover towers.

c. Ditto (notice the slightly inferior yield and greater waste of water, with somewhat less chamber-space).

d. Poor pyrites, small works, no Gay-Lussac or Glover tower. Average of a year.

e. Same works, during the hottest month.

f. Same works, when burning less pyrites in the same chamber-space as before.

Sorel remarks that the just-quoted statements of Naville's do not represent the present results obtained at the best French works. At one of the apparatus at l'Oseraie during the first 10 months when the Glover and Gay-Lussac towers had to be supplied with acid, and all the chambers with nitre, the yield was 143.3 H_2SO_4 for 100 parts of 50-per-cent. pyrites, with an expenditure of 1.03 kilog. nitre per 100 H_2SO_4 , and an average make of 3.359 kilog. H_2SO_4 per cubic metre (that is, rather more than 14 cubic feet per lb. of sulphur burnt). At the end of the year the same apparatus made 4.128 kilog. per cubic metre (=only 11.5 cubic feet of chamber-space per lb. of sulphur burnt!); the yield was 148.81 kilog. H_2SO_4 per 100 kilog. 50 per cent pyrites, with 0.8 per cent. sulphur left in the cinders. This means 301.2 H_2SO_4 per 100 sulphur burnt, and 0.75 nitre per 100 H_2SO_4 , or 2.26 commercial nitre per 100 sulphur burnt. These figures, which Sorel took from the books of the Saint-Gobain Company,

are certainly in every respect astonishingly much better than anything I have heard of elsewhere from the best-managed works, let alone the remarkably small chamber-space, and I must confess that I do not understand the possibility of such results.

Kienlen (*Monit. scient.* 1889, p. 1238) makes the following statements concerning the work done at the best French factories in the year 1889. With good pyrites and properly constructed apparatus, the yield on 100 parts of sulphur *burned* is 295 H_2SO_4 . 100 parts of pyrites leave about 68 parts of cinders, with an average percentage of 1 per cent. sulphur. With Sain-Bel ore of 51·5-per-cent. S, 100 parts of pyrites will yield $2\cdot95 \times (51\cdot5 - 0\cdot68) = 150$ parts of monohydrated sulphuric acid, corresponding to a yield of 291 H_2SO_4 on 100 S in the pyrites *charged*. There is thus a loss of $15\cdot25 \text{ H}_2\text{SO}_4$, or 4·97 per cent., the sulphur being used up as follows:—

Recovered in the shape of H_2SO_4	95·03
Lost in the exit-gases	3·65
Lost in the cinders	1·32
	<hr/>
	100·00

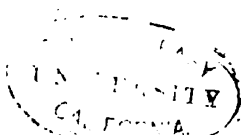
The consumption of nitrate of soda in the best works averages 0·90 for 100 monohydrate produced = 1·35 for 100 pyrites, or 2·60 for 100 sulphur charged. This is obtained even with “forced work,” where 1 cubic metre of chamber-space is made to yield 3·5 or even 4 kilog. of H_2SO_4 in 24 hours.

I have been favoured by the firm of Ernst Güssefeldt, of Hamburg, with the originals of six years’ returns of the acid-works at Hamburg and at Kastrup (near Copenhagen), with permission to publish the results. We here give the averages taken from the six years’ returns (1884–1889), which at the same time give a very good example of the way of stating the yields.

A. Hamburg works.

Description of Pyrites: Rio Tinto.

Average quantity burnt per annum	2775·6 tons.
„ percentage of sulphur in pyrites.....	48·8 p. c.
„ quantity of sulphur in pyrites bought ...	1354·6 tons.
„ „ acid 106° produced	6322·2 „



The same reduced to real H_2SO_4	3948·2	tons.
Sulphur contained in acid produced	1290·0	"
" lost.....	64·6	"
Per cent. sulphur lost in cinders *	2·69	p. c.
" " " chamber-process	2·03	"
" " " lost altogether	4·71	"
95 per cent. nitrate of soda consumed, total.....	50·9	tons.
Ditto, per cent. of sulphur	3·75	p. c.
Ditto, per cent. of acid 106° Tw.	0·80	"
Real H_2SO_4 made per 100 pyrites.....	142·5	"
" " sulphur	291·9	"

B. *Kastrup works.*

Pyrites burnt per annum (average)	1896·2	tons.
Sulphur in pyrites (average)	49·2	p. c.
" " per annum (average)	932·8	tons.
Acid 106° produced per annum (average).....	4215·2	"
" calculated into real H_2SO_4	2534·5	"
Sulphur contained in acid produced	860·2	"
" lost altogether	71·9	"
" " in cinders	6·85	p. c.
" " in chamber-process	0·90	"
" " total	7·75	"
95 per cent. nitrate consumed (average)	22·92	tons.
" " per 100 sulphur	2·41	"
" " " acid 106° Tw.	0·50	"
Real H_2SO_4 made per 100 sulphur	282·9	"
Coals used per annum (average)	309·4	tons.

The remark is added that the possible errors in stock-taking through inaccuracies of tables and so forth, taking them all as increasing the real yields, cannot possibly in the aggregate amount to more than 4 parts of H_2SO_4 per cent. of sulphur, so that, for instance, the *minimum* quantity really made at the Hamburg works, in lieu of 291·9, might be 288 per cent. of the sulphur.

* The quantity of sulphur found in the cinders was from 2·8 to 4; there was 70 cinders assumed per 100 green ore.

Cause of the Losses in Manufacturing Sulphuric Acid.

The causes of the *loss of nitre* have been mentioned in detail, p. 629. They are (1) loss of nitre-gas carried into the outer air, (2) nitrogen compounds left in the chamber-acid, (3) nitre-gas reduced to N_2O or N .

The *loss of sulphuric acid itself* arises from the following causes :—

1. Incomplete combustion of the sulphur (loss in the cinders) ; this has also been spoken of before (p. 233). With brimstone this loss is not worth mentioning ; with pyrites it is so much the greater the poorer the ores are, and besides it varies enormously according to the construction of the burners and the care with which they are worked, from 1 to 10 parts and more of sulphur per 100 pyrites, or from 2 to 30 per cent. of the total sulphur. A portion of the sulphur is sublimed, and is found in the connection-pipes and in the acid itself, and is a clear loss.

2. Losses of SO_2 by leakages of burners, pipes, chambers, &c. By bad draught much loss may occur, since then at the doors of the burners, nitre-ovens, &c., the gas continually blows outward. Bad pipe-joints, but especially chambers worn down too much, lead to great losses. I have seen chambers which, when ultimately stopped, presented in their interior the image of the starry sky from the innumerable holes in the top ; and Wright (Chem. News, xvi. p. 93) has independently used the same simile. Many manufacturers have no idea of the great loss which they suffer in this way, by allowing, from motives of ill-timed economy, a chamber to go on too long and trying to patch it up. Wright found in a chamber system that went three years without repairs :—

	Nitre for 100 parts of sulphur burnt.	Cubic metres of chamber- space per kilog. of sulphur burnt per diem.	Practical yield (theoretical = 100).
First year	9.31	1.150	81.5
Second year ...	9.84	1.073	75.4
Third year	10.02	1.017	68.4

3. Losses of SO_2 by *incomplete conversion into sulphuric acid*. Extremely little SO_2 can remain dissolved in chamber-acid if there is an excess of nitrous compounds present ; the greater portion of

any remaining SO_2 escapes from the chambers into the outer air. The reason of this may be irregularity of the process in general, want of nitre, insufficient chamber-space, insufficient draught, &c., as explained in detail previously. The losses from this source are nearly always much greater where the nitre is not recovered, for the reasons stated above. The very widely divergent statements on the yield of sulphuric acid are explained to a great extent from this cause alone.

Statements of Costs for the Manufacture of Sulphuric Acid.

1. *From brimstone.*

At Marseilles, 1867 (Kerl-Stohmann, iv. p. 1495).

	francs.
1000 kilogs. brimstone	170·00
75 „ nitrate of soda, @ 40 francs ...	30·00
100 „ coals.....	2·50
Wages	4·00
General expenses	6·50
	<hr/>
	213·00

Yield 4000 kilogs. acid of 53°B. ($=115^\circ \text{Tw.}$), which thus cost 5·32 francs per 100 kilogs.

In America (*districts of New York and Philadelphia*) according to the 'Mineral Resources of the United States' for 1886, p. 671.

1 ton (2000 lbs.) of brimstone thirds (98 per cent.)	\$19·00
50 lb. nitrate of soda, at $2\frac{1}{2}$ cents per lb.	1·25
5 cwt. coal at \$4 per ton	1·00
Wages	2·25
Superintendence and management.....	2·00
General jobbing repairs	·50
Interest on capital (\$75,000) at 10 per cent. (for 20 tons acid daily)	4·60
	<hr/>
	\$30·60

Produce= $4\frac{1}{2}$ tons acid of 50°Baumé , cost per ton ... \$6·80

[Therefore cost of one ton of real H_2SO_4 in the shape of chamber-acid=\$10·60 or about £2 3s.]

The following cost-sheet for brimstone-acid at an American works has been supplied to me from a thoroughly authentic source; it refers to the year 1888:—

Brimstone, 1,637,127 lb.	\$19,070·00
Nitre, 91,057 lb.	1,858·00
Sulphuric acid 60° B., 80,380 lb.	402·00
Labour for operating and repairs	2,096·81
Office expenses	3,100·00
Coal, 454 tons (at 22·40 lb.)	463·00
Oil, tools, &c.	240·00
Repairing materials	688·00
Depreciation of buildings, furnaces, and chambers, at 50 cts. per ton of acid produced ...	1,721·00
Ditto of machinery, boilers, &c., at 10 cts. ...	344·00
Insurance	775·00
Interest 6 per cent. on \$60,000	3,600·00
Ground-rent	204·00

\$34,561·81

Sulphuric acid 60° Baumé produced 6,885,373 lb.

Cost of 100 lbs. acid 60° Baumé 50·2 cents.

N.B.—The nitre-cake, having very little value in America, is not taken into account. The consumption of nitre at that works was unusually high (5 per cent. on the sulphur), owing to the small size of the Gay-Lussac tower.

2. *From pyrites.*

In Belgium, 1877, according to Lacroix (Kerl-Stohmann).

	francs.
1000 kilogs. pyrites, with 35 per cent. sulphur	35·00
42 „ nitrate of soda, @ 38 francs.....	15·96
150 „ coals, @ 1·20 franc	1·80
Wages	3·00
General expenses, repairs, &c.	3·00
	<hr/>
	58·76

Yield 1365 kilogs. acid of 53° B.=4·30 francs per 100 kilogs.

In France, 1876, according to Favre ('Moniteur Scientif.' 1876, p. 273).

	francs.
640 kilogs. pyrites of 35 to 40 per cent. S., @ 30 francs	19·20
18 „ nitrate of soda, @ 38 francs	6·84
30 „ acid of 144° Tw. for decomposing the nitrate, @ 30 francs	1·20
80 „ coals, @ 30 francs	2·40
Stone-breaking and other manual labour ...	3·26
Repairs and general expenses	5·00
	<hr/>
	37·90
Deduct 20 kilogs. nitre-cake, @ 5 frs.	1·00
	<hr/>
Cost of 1000 kilogs. sulphuric acid of 50° B. (= 106° Tw.)	36·90

(The strength is calculated from Vauquelin's tables, and corresponds to 66 per cent. of SO_4H_2 .)

In England I have found (at my own or neighbouring works) the cost per ton of SO_4H_2 :—

a. From 40-per-cent. Belgian small pyrites burnt in a muffle furnace :—

	£	s.	d.
1·048 ton pyrites, @ 18s. 8d.	0	17	5·600
0·044 „ nitre, @ £15	0	6	7·200
0·557 „ coals, @ 4s. 6d.	0	2	6·079
Sundry tools, materials for repairs, &c.	0	3	5·586
Wages: a. regular	0	6	2·186
„ b. extraordinary (repairs &c.)	0	1	7·044
		<hr/>	
		1	17 9·695
Deduct value of acid nitre-cake	0	1	1·200
		<hr/>	
Cost of oil of vitriol per ton	1	16	8·495

b. From Norwegian and Westphalian lump ore (without Gay-Lussac tower) :—

	£	s.	d.
0·9795 ton of pyrites (containing 0·4165 ton of sulphur), @ 23 <i>s.</i> 6½ <i>d.</i> ...	1	3	0
0·0893 „ nitre, @ £16	0	12	7
0·1250 „ coals, @ 4 <i>s.</i>	0	0	6
Wages	0	7	5
Materials, repairs, &c.	0	2	0
	2	5	6
Deduct value of nitre-cake.....	0	1	6
Cost of oil of vitriol per ton	2	4	0

c. From cupreous Norwegian pyrites, with Gay-Lussac and Glover tower, in 1873 :—

	£	s.	d.
0·838 ton of pyrites (with 0·38 ton of sulphur), @ 25 <i>s.</i> 6 <i>d.</i> ...	1	1	4·428
0·0172 „ nitre, @ £12	0	4	1·536
0·171 „ coals, @ 10 <i>s.</i>	0	1	8·520
Wages for the process itself	0	6	9·520
Repairs (including wages)	0	0	10·464
Renewal of chambers (spread over the acid)	1	0	

Cost per ton of oil of vitriol..... 1 15 10·468

(N.B.—The coals did not include those used for pumping the acid.)

d. From cupreous Spanish pyrites, in 1876 :—

	£	s.	d.
0·758 ton of pyrites (with 0·364 ton of sulphur), @ 19 <i>s.</i>	0	14	4·80
0·0145 „ nitre, @ £11	0	3	2·28
0·250 „ coals, @ 4 <i>s.</i>	0	1	0·00
Wages for the process	0	3	6·00
Repairs	0	0	6·00
Renewal of chambers.....	0	1	0·00
	1	3	7·08

In all these cases the acid obtained was of 140° to 144° Tw.; the cost of concentrating it further has been mentioned previously (pp. 692 & 693).

This becomes almost certain by the following statement, which I have received from the most authentic possible source. It refers to an old-established German works and to the year 1889. (The "Mark" may be taken as slightly less than a shilling.)

Cost of 1000 kilog. (=a ton) of real H_2SO_4 in the shape of acid of 142° Tw.

702 kil. pyrites 47 per cent. at M. $1\frac{1}{2}$ per 100 kil. =	M. 10·53
13·1 „ nitrate of soda at M. 20	2·62
132 „ coals at M. 1	1·32
Wages for process	3·36
Repairs of buildings and apparatus	1·81
General expenses and management	2·56
	<hr/>
	22·20

This does not comprise amortization of the plant, for which about 3 M. per ton must be charged, making the total = M. 25·20, or rather less than 25s. per ton of H_2SO_4 , exclusive of packages.

Sorel gives the following statements concerning the cost-price of acid of 50° B. (=106° Tw.) at l'Oseraie (comp. p. 760), in November 1885:—

	Quantities.		Price.	Amount.		Total.	
	Total.	Per 100 kil. acid.		Altogether.	Per 100 kil.	Altogether.	Per 100 kil.
	kil.		fres.	fres.	fres.	fres.	fres.
Superintendence	285-00	0-03	1,484-70	0-16
Our	1199-70	0-13		
Tests	374,550	42-00	26-00	9738-30	1-09	11,191-90	1-25
Sulphuric acid 36° B.	5,409	0-61	26-58	1455-66	0-16		
.....	87,850	9-85	21-50	1888-75	0-22	1,888-75	0-22
Shipping	302-20	0-04	770-70	0-09
Freights	30-00	"		
Cost of strange } shinings	438-50	0-05		
Repairs	587-75	0-07	587-75	0-07
Wear and unfore- } seen expenses	631-00	0-07	631-00	0-07
Subtotal : Items sent out	258,500	28-98	3-00	775-50	0-09	16,554-86 775-50	1-86 0-09
Grand total 891,821 kil. acid 50° B.						= 15,779-36	1-77
Grand total 557,388 kil. H ₂ SO ₄							= 2-83

There was produced for 100 kil. 50 per cent. pyrites : 148·81 H_2SO_4 .

Commercial nitrate expended per 100 H_2SO_4 : 0·74.

„ „ „ „ 100 pyrites : 1·11.

To the above items of expenditure should be added the amortization of the plant, the cost of which is detailed further on, taking the buildings per year at $\frac{1}{20}$ cost-price, furnaces, chambers, towers, &c. at $\frac{1}{10}$, steam-boilers and engines at $\frac{1}{3}$ cost-price, which comes to 31,647 francs per year in all, or 0·527 franc per 100 kil. H_2SO_4 for the first 4 years, 0·39 frc. from the 5th to the 9th year, 0·09 frc. from the 10th to the 20th year. (We cannot admit that the amortization should be calculated at such a low figure from the fifth year onward, as the depreciation of the furnaces, chambers, boilers, &c. must needs to be taken into account, and the "amortization" should include the sums necessary to provide for their renewal.)

Sorel gives the following figures as the actual cost-price of apparatus at l'Oseraie (France), apart from the value of land :—

1. *Buildings.*

	franca.	cent.
Chamber-sheds (all brickwork).....	50,700	90
Furnace-shed „	15,147	15
Steamboiler-shed „	9,269	10
Foundations and timber-work for Glover and Gay Lussac	14,604	35
Main flue	3,940	55
Chimney (2 metres inside, 40 m. high)...	13,088	35
	<hr/>	
	106,750	40

2. *Apparatus.*

	franca.	cent.
Pyrites-burners	31,686	70
Glover tower	26,188	75
Chambers (4500 cub. metres = nearly 160,000 cubic feet)	74,131	80
2 Gay Lussacs, 20 metres high	22,804	10
Exit-gas tube	6,157	15
Steam-pipes	4,541	25
Acid-tanks and acid-eggs	15,144	55
Tools	943	05
	<hr/>	
	181,597	35

3. *Steam-boilers and engines.*

	francs.	cent.
2 steam-boilers and setting	21,267	60
1 air-pump and pipes.....	9,167	15
1 water-pump and pipes	7,114	55
1 fan-blast and driving-engine	3,192	50
	<hr/>	<hr/>
	40,741	80
	<hr/>	<hr/>
Grand total.....	329,089	55

This apparatus is capable of making 6000 tons of O.V. per annum, with the "forced work" frequently alluded to, viz. a chamber-space of only 11 or 12 cubic feet per lb. of sulphur burnt. This is made possible by the extraordinarily great size (and cost) of the nitre-recovery apparatus. If this had been made of the usual dimensions, the cost would have been about 38,000 frcs. less, but then the production, at the usual rate of 2.25 kg. per cubic metre (say about 21 cubic feet per lb. of sulphur), would have been only 3600 tons per annum.

I have received the following altogether authentic account of the cost of making sulphuric acid at a first-class English alkali-works for the 12 months ending Dec. 31, 1889.

One ton of real O.V. (H_2SO_4), in the shape of acid of 148° Tw., required on the yearly average:—

	£	s.	d.
14.12 cwt. pyrites, at 11.8s. per ton	0	8	4.0
27.06 lb. nitre, at £9 9s. per ton	0	2	3.4
5.30 cwt. coals, at 5s.	0	1	3.9
Process wages	0	3	3.7
Repairs (incl. wages)	0	4	4.1
General expenses and salaries.....	0	2	1.0
Sundries	0	1	4.4
	<hr/>	<hr/>	<hr/>
	£1	3	0.5

The pyrites used was Spanish ore, testing on an average 49.55 per cent. sulphur. The yield of real H_2SO_4 on the sulphur bought was=286 per cent., on the sulphur burnt=exactly 300 per cent. (calculated by Kolb's table). The chamber-space was rather more than 16 cubic feet per lb. of sulphur.

For America the following calculations of the cost-price of pyrites-acid is given in the United States 'Mineral Resources' for 1886, p. 671 :—

2½ short tons of pyrites (46 per cent.), at 10 cents } per unit per ton	\$11·50
60 pounds nitrate of soda, at 2½ cents.....	1·50
5 cwt. of coal, at \$4 per ton	1·00
Wages	3·00
Superintendence and management	2·00
General jobbing repairs	0·60
Interest on capital of \$100,000 at 10 per cent. ...	6·15
	<hr/>
	\$25·75
Produce 4½ tons of 50 Baumé, cost per ton	\$5·50

CHAPTER XIV.

BY-PRODUCTS OF THE MANUFACTURE OF SULPHURIC ACID.

THE most important of these in the case of cupreous pyrites is the copper itself, along with the iron oxide (obtained in this case in a sufficiently pure form), sometimes also with silver; we shall go into this in detail afterwards. From non-cupreous pyrites, however, iron and zinc are only exceptionally obtained. We do not, of course, refer to metals whose production is the principal object of the whole process.

Besides, thallium and selenium may be mentioned as by-products of sulphuric-acid making.

The cinders from non-cupreous pyrites (as to their composition comp. p. 235) are frequently used *as ballast for making roads*; they yield very firm, dry, and even roads, which, however, are soon ground into dust by the traffic of vehicles, and in wet weather are then very muddy. Besides, the rain-water washes out iron and zinc sulphates, and may carry these into neighbouring wells (Sarrazin, 'Archiv der Pharmacie,' ccix. p. 418).

These cinders have frequently been proposed for the *absorption of sulphuretted hydrogen gas*, and really seem to have been here and there employed for purifying coal-gas and for disinfecting cesspools (Zeitsch. für chem. Grossgew. i. p. 70). This, however, cannot be done extensively, as the cinders do not act any thing like so energetically upon H_2S as precipitated ferric hydroxide or bog-iron-ore, and therefore the purifying-apparatus would have to be made of enormous dimensions. Probably more success will be obtained in the manufacture of copperas for neutralizing the sulphuric acid formed in the oxidation of bituminous lignite slates; formerly metallic iron used to be employed for this purpose.

It has also been proposed to utilize the pyrites-cinders or the "purple ore" (see below) for decomposing solutions of alkaline sulphides, but in this case the action is too imperfect. But after converting the ferric oxide into a "ferrite" by ignition with soda, the compound thus formed has an energetic action upon solutions of alkaline sulphides, upon which are founded the processes of Arrott and of Ellershausen (comp. Vol. II.).

Iron.—Formerly ordinary pyrites-cinders (from non-cupreous ores) could not be employed for making iron, because they contained at least 4 per cent., and usually more than this, of sulphur. One of the first attempts at utilizing such cinders for the manufacture of iron was made at the Chauny works, which, in 1873, exhibited iron made from non-cupreous pyrites-cinders, desulphurized by repeated roasting in a Perret's kiln in thin layers. For this purpose the plates of this kiln were charged alternately with cinders and with fresh pyrites, the heat produced in the burning of the latter causing a supplementary roasting of the cinders (Hofmann's 'Bericht,' 1875, i. p. 164).

Since that time very much progress has been made in treating the pyrites, both lumps and smalls, in such manner as to desulphurize it more completely; but this can only be done if the ore is pure, *i. e.* containing very little or no zinc and lead sulphides. Such pure ores can be burned in lumps down to 2.5 or even 2 per cent., and in the shape of dust even below 1 per cent. sulphur in the cinders, and in this case they can be smelted like ordinary (somewhat impure) iron-ores.

It has frequently been attempted to employ the cinders of small ore in larger quantities for smelting in a blast-furnace without stopping it up, by conglomerating them in different ways, but without much success. A patent has been taken out by J. Cahen for this purpose (10th June, 1875). He moulds the cinders into suitable cakes with tar, peat, and limestone, and smelts these in a blast-furnace; the pig-iron is said to be very pure, the sulphur being absorbed by the lime, and the peat assisting in the formation of volatile phosphuretted hydrogen (?). J. L. Bell also moulds the small ore with lime into bricks, which gain hardness by drying, and uses them in a blast-furnace. All such artificial conglomerates are soon crushed by the great pressure in the blast-furnace, and thus act like the loose powder.

Richters (Dingl. Journ. xcix. p. 292) pursued the application

of pyrites-cinders in a coke blast-furnace by the analysis of all the products. With a charge of 38 calcined magnetic iron-ore, 1½ black band, and 25·5 cinders (composed as on p. 326—that is, containing 4·35 per cent. SO_3 and 1·53 S in other forms), and 35 limestone, under especially favourable circumstances, pig-iron with only 0·022 per cent. of sulphur was obtained; when, however, the temperature was lower, even with only 12 pyrites-cinders to 53·5 other iron-ore and 33·5 limestone, the pig-iron showed 0·049, 0·088, 0·096, 0·224 per cent. of sulphur. With a mixture of 19·2 pyrites-cinders, 46·5 other iron-ores, 30·1 limestone, and 4·2 potsherds the sulphur in the pig-iron varied from 0·033 to 0·060 per cent.; by adding another 3·77 potsherds the sulphur was increased to 0·110–0·146 per cent. The pig-iron poorer in sulphur always contained a great deal of silicon, up to 3·485 per cent.

The cinders from roasting Schwelm pyrites are said to furnish an excellent material for Bessemer pig, as they contain very little phosphorus and copper, which are so injurious to the quality of steel. F. Schmidt (Berg- u. hüttenmänn. Zeit. 1878, p. 68) states the composition of these cinders as follows:—

Ferric oxide	90·547	} = 65·0056 Fe.
Ferrous oxide	0·520	
Iron bisulphide.....	0·574	
Lead sulphide	0·142	
Copper sulphide	0·026	
Manganous oxide	0·463	
Alumina	1·448	
Lime	0·388	
Magnesia	0·220	
Sulphur trioxide	1·110	
Phosphorus pentoxide	0·035	
Silica.....	3·447	
Moisture	0·897	
<hr/>		
99·817		

Paur (Germ. Patent, No. 8730, May 22, 1879) proposes to treat the crushed pyrites-cinders with a solution of alkaline permanganate, by which sodium-sulphate and MnO_2 are formed. The first is washed out; and the residue forms a manganiferous iron-ore, free from sulphur (but in all probability far too expensive).

Arnois (Amer. Pat. 413,428) seeks to convert burnt pyrites into a useful paint by treating it at a dark red heat in an ordinary atmosphere with a mixture of calcium carbonate and common salt in various proportions. (No doubt the treatment applied to the residue from the manufacture of Nordhausen acid (Chap. XV.) could be applied to pyrites-cinders as well; but only in the case of very pure ores, like the Aguas Tenidas, can products be obtained of sufficient purity for the above-named purpose.)

Zinc.—Pyrites containing zinc, such as the Westphalian ore from Meggen, cannot possibly be desulphurized in the burners so well as purer ore, owing to the great heat required for decomposing the zinc sulphate. The cinders from such ores contain both too much sulphur and too much zinc to be useful for the manufacture of iron without a special treatment for removing these impurities.

P. W. Hofmann ('Zeitschr. d. Vereins deutscher Ingenieure,' xviii. p. 521) has proposed the following process for utilizing the cinders from Westphalian pyrites, which sometimes contain 6 per cent. of zinc. The cinders contain the zinc as sulphate, which is only decomposed at a much higher temperature than is attainable in a pyrites-burner. The zinc sulphate can be washed out by water at 40°; but it contains too much iron sulphate to be saleable. If, however, a solution of 1.25 sp. gr. be mixed with a proportion of NaCl equivalent to the sulphuric acid contained in it, and heated to 30° C., a lye of 1.38 sp. gr. is obtained, from which, on cooling, such a quantity of Glauber's salt crystallizes that this alone pays all expenses. The mother-liquor contains chloride of zinc with more or less common salt and the sulphates of iron, zinc, and sodium. If evaporated to 1.60 sp. gr., all foreign salts are separated, and a solution of zinc chloride, with mere traces of sulphates and of iron, remains behind, which can be employed directly for pickling railway-sleepers. The residue from lixiviating the sulphates is allowed to lie a few days in the air to dry; most of it then falls to powder. When this is passed through a sieve, the fine dust is found to be almost free from sulphur, the rougher particles containing nearly all the sulphur in the shape of FeS. The dust might be employed in a blast-furnace.

At the Aussig works formerly the crude zinc sulphate obtained in just the same way was worked up by the addition of calcium

chloride (waste lye from the recovery of sulphur) into "pearl hardening" and zinc chloride. Owing to the want of a sufficient market, this manufacture has been discontinued.

Creutz (Chem. Ind. 1883, p. 258) remarks that Hofmann's process has not been much used, because the reactions are not as smooth as represented. The sodium sulphate remaining in the zinc-chloride liquor is prejudicial to its employment for pickling timber. Nor were better results obtained by mixing the solutions of sodium chloride and zinc sulphate in the cold, as recommended by the American patent No. 236,051. The formation of double salts of zinc and sodium is the cause of this difficulty. It is therefore best to employ calcium chloride (comp. above) in the following manner:—The pyrites-cinders are exposed to the weather as long as possible to oxidize the iron and manganese compounds and the sulphurous acid. They are then lixiviated with cinders containing 3 per cent. zinc; a solution of zinc sulphate is obtained of spec. grav. 1.16, containing next to no iron and only traces of manganese and cobalt. This liquor is mixed with waste calcium-chloride liquor from the Weldon process, of spec. grav. 1.116, leaving a small excess of zinc sulphate. Calcium sulphate is precipitated and is filtered off. The clear liquor, of spec. grav. 1.075, is boiled down in an iron pan with top heat, and a little bleaching-powder is added to precipitate manganese and cobalt as peroxides. At a concentration of 1.5, the last traces of calcium sulphate are precipitated, and the clear liquor now contains only zinc chloride with a little zinc sulphate, no more than is contained in the liquor obtained by dissolving scrap zinc in commercial hydrochloric acid. This process has the drawback of requiring fuel for boiling down the liquor, but it furnishes a liquor entirely fit for pickling wood. The expense of boiling down is saved when the crude solution of zinc chloride is treated for the preparation of zinc hydrate (for purifying soda liquors from sulphides) by addition of lime, and filtering through a sand filter.

Egestorff's Salzwerke (G. P. 23,712) purify pyrites-cinders from zinc by weathering, lixiviating, adding to the liquor calcium or barium carbonate, and treating it with a current of air. In this case the iron is quickly precipitated, and there is obtained on the one hand an iron-ore free from zinc, on the other hand zinc salt free from iron.

The Königshütte Berg- und Hüttenverwaltung (G. P. 28,465)

roast pyrites-cinders, containing zinc, with common salt, and lixivate with weak hydrochloric acid. The liquor in case of need is freed from copper and is cooled down to such a temperature that sodium sulphate crystallizes out. The zinc remains in the mother-liquor, and is recovered in the usual manner, probably chiefly in the shape of crystallized zinc sulphate.

Kosmann (Fischer's *Jahresb.* 1886, p. 268) considers all the processes hitherto employed for the above purposes as of doubtful economic value.

Herberts (G. P. 38,780) treats pyrites-cinders containing zinc in an iron boiler under pressure with steam; the sulphates of zinc and iron are dissolved, ferric oxide remains behind. Another patent of the same inventor (G. P. 41,333) contains some improvements.

Riemann (G. P. 38,072, Fischer's *Jahresb.* 1887, p. 510) contends that only a third part of the zinc is dissolved in this manner. He therefore returns to the roasting with salt, but adds ferric sulphate, obtained by treating ground pyrites-cinders with hot sulphuric acid. A mixture is made of the cinders with 8 or 10 per cent. of crude ferric sulphate, and 15 or 18 per cent. of common salt, and is roasted for several hours in a reverberatory or muffle furnace, with access of air, at a temperature not exceeding 500° C. The product can be lixiviated with water alone, without adding any acid; the washed residue contains only 1 or 1.5 per cent. zinc, 0.3 or 0.6 sulphur, and 55 iron, and is therefore a useful iron-ore. The liquor contains any copper present in the ore, zinc chloride, and sodium sulphate. These salts cannot be separated, as asserted, by boiling down to spec. grav. 1.53, owing to the formation of double salts of zinc and sodium, but by concentrating the liquor, when at spec. grav. 1.32 to 1.36, in the cold by means of a vacuum. It is claimed that this process really permits of utilizing the cinders from German pyrites, hitherto so troublesome.

Electricity has also been invoked for precipitating the zinc from the liquors obtained by the above-mentioned processes, but this does not seem to be economical.

Perino (G. P. 46,748) makes an intimate mixture of the ore with ferric nitrate, and exposes this to gentle heat; about 50° nitrous fumes are evolved and zinc sulphate is formed, whilst the iron sulphide is less easily acted upon. The process is finished at

about 150° or 200°. [It seems very hopeless to expect it to pay, even when the nitrous fumes are treated for recovery of nitric acid.]

Thallium.—In the flue-dust and the chamber-deposit of many descriptions of pyrites the rare metals *selenium* and *thallium* have been found. The former has hitherto no industrial application, apart from the employment of crystalline selenium in photometry, as its electrical conductivity changes in proportion to the intensity of the light that falls upon it.

Thallium, however, is manufactured on a comparatively large scale at Aussig and Mannheim; and it might possibly be found useful for optical glass, replacing the alkali; owing to its very high atomic weight (204) it gives, along with red lead and quartz, the specifically heaviest and consequently the most refractive glass hitherto known (Lamy).

The preparation of thallium from the flue-dust of Westphalian pyrites has been described by Schaffner (Wagner's Jahresb. 1871, p. 1). The flue-dust was collected in a large brick chamber without being exposed to the action of nitrous vapours, the chambers being fed directly with nitric acid. It is coloured by ferric oxide, contains much arsenious acid, ferric sulphate, some zinc oxide, lead oxide, traces of antimony and silver, thallium sulphate, &c. Carstanjen (Wagn. Jahresb. 1868, p. 10) found in it 3·5 per cent. thallium. On the sides of the chamber crystals were found of the compound As_2O_3 and SO_3 , discovered by Reich. The flue-dust is lixiviated by boiling with steam, with the addition of a little sulphuric acid, as a portion of the thallium seems to be present as basic sulphate, which would escape solution. After settling, the clear portion is siphoned off and filtered through calico; the residue is boiled again. From the liquid the thallium is precipitated as protochloride. The very impure reddish precipitate is washed with cold water and converted into sulphate by hot concentrated sulphuric acid, the heating being continued till all excess of acid is driven off. The sulphate is dissolved in water, filtered, and again precipitated by hydrochloric acid, the TiCl now being separated almost in the pure state. If it is not yet pure, especially if it contains arsenic, the operation must be again repeated. In order to remove all arsenic, sulphuretted hydrogen is conducted into the solution of thallium sulphate,

which precipitates all the arsenic with small quantities of thallium; the latter is precipitated from the filtrate by hydrochloric acid as perfectly pure TlCl , and converted into sulphate as above. The latter is reduced to metallic thallium by digesting its solution in a porcelain or stoneware dish with metallic zinc. The spongy metal obtained is washed with distilled water, pressed between blotting-paper, and melted in an iron or porcelain crucible, hydrogen or coal-gas being conducted through to prevent any oxidation; the heat should not be too strong, because it might volatilize the thallium. The melted metal, similar to mercury, is cast into small rods in paper moulds. It should be kept in boiled water free from air, the glass being closed whilst the water is boiling; but even then the latter after a short time shows an alkaline reaction. It is best kept in a solution of zinc sulphate. It can also be obtained well crystallized by Woehler's process, viz. by suspending in the thallium solution a beaker with its bottom cut off, and its lower part closed with bladder tied round: this is filled with water up to the level of the solution outside; a zinc plate is hung up in the water, and the latter connected with a platinum wire, which dips into the thallium solution and is bent into a spiral below the bladder.

Krause (Dingl. Journ. cexvii. p. 323) observes that the treatment of thallium protochloride with concentrated sulphuric acid is very unpleasant work in large quantities. He has found that the decomposition can be quickly and completely effected by a weak solution of Glauber's salt, say 4° to 7° Tw. He lixiviates the fine dust in a cask with water and steam, siphons off the settled liquid into a second cask, and adds to this solution of thallium sulphate hydrochloric acid; the TlCl subsides very quickly, if the liquid is well agitated, for instance by a current of air. After a short rest the clear liquid is run off, the cask is filled up with pure water, heated by steam, and crystallized sodium sulphate added till the solution shows 7° Tw. After strong agitation the decomposition is complete, and the liquid is siphoned off into a third cask, which is placed somewhat lower; here it is acidulated with sulphuric acid, and the thallium precipitated by zinc. Similarly to Schaffner, he washes the sponge with water free from air, presses and melts it. This process permits working continuously and without contact with fire.

Nietzki has made very detailed communications on thallium

(Wagner's Jahresb. 1876, p. 4). He found in the flue-dust of the Duisburg chemical works, where Westphalian pyrites is used, 0.1 to 0.2, sometimes even 1 per cent. thallium. The precipitation as TlCl is incomplete: it is true that TlCl , which is soluble in 500 parts of water, is much less so in the large excess of hydrochloric acid actually employed; but there remains even then 10 per cent. of the thallium present in the mother-liquor. Much more complete is the precipitation of thallium by potassium iodide as TlI , even from very dilute solutions of flue-dust. Therefore both the mother-liquors from the TlCl precipitate and the dilute extractions of flue-dust are afterwards treated with KI . By boiling the TlI with sodium sulphide the iodine is recovered as NaI ; and the insoluble Tl_2S is worked up for Tl_2SO_4 along with the TlCl . From the sulphate the thallium is obtained by electrolysis, to avoid its contamination with zinc. In this case crude thallium sulphate can be employed; whilst direct reduction with zinc is troublesome, owing to the evolution of arseniuretted hydrogen and the reduction of ferric salts, the ferrous sulphate soon forming a crust over the zinc and making it inactive. Nietzki even employs KI for volumetrically estimating thallium; but the solutions must not be too dilute.

Stolba's process (Wagner's Jahresb. 1874, p. 1), allowing a thallium-alum or thallium-iron-alum to crystallize from concentrated solutions of flue-dust, is only adapted for a substance extraordinarily rich in thallium.

Woehler (Ann. Chem. Pharm. clxiv. p. 74) states that thallium is more simply produced by fluxing the chloride with sodium carbonate and carbon. 20 parts TlCl , 8 parts of dry Na_2CO_3 , and 1 part of lampblack are mixed together and fluxed in a fire-clay crucible at a moderate red heat. A small loss occurs by some chloride volatilizing; this can be avoided by stirring up the mixture with water, drying, and then fluxing.

Selenium was discovered (in 1817) by Berzelius in the chamber-deposit of the sulphuric-acid works at Gripsholm, at which Fahlun sulphur (obtained in roasting ores) was used. It also occurs in volcanic sulphur, *e. g.* 0.264 per cent. in the solfataras of Naples, according to Phipson (Chem. News, v. p. 337),—principally, however, in many descriptions of pyrites; so that the chamber-deposit of the Mansfeld and Oker works is the best source of it. Selenium occurs in several allotropic modifications, in regard to which we

must refer our readers to the chemical treatises. Its spec. grav. is given as 4.26 to 4.8, melting-point 400° , boiling-point about 700° . Selenium always occurs in very small quantities; but its characteristic reactions cause it to be easily discovered, and it becomes very much concentrated in the deposit of flue-dust. Some Harz works' deposit is said to contain 10 per cent., that of the Eisleben works 9 per cent. of selenium; annually several cwt. are obtained in this way (Böttger and Kemper, Wagner's 'Jahresb.' 1860, p. 169). On selenium in French sulphuric acids communications have been made by Kuhlmann, Personne, and Scheurer-Kestner (ib. 1872, p. 246); comp. also Lunge (Chem. Ind. 1883, p. 128) and Davis (J. Soc. Chem. Ind. 1883, p. 158).

The deposit contains free selenium, as the selenious acid formed by burning is reduced by sulphurous acid. Otto (Lehrbuch d. Chem. 4th ed. i. p. 633) digests the deposit, previously washed with water, with aqua regia to oxidize the selenium, adds sulphuric acid, evaporates to dryness, driving off the other acids, treats the residue with water, and from the solution, by cautious addition of ammonium sulphite, first precipitates white mercurial chloroseleniate, then from the filtrate, by more ammonium sulphite and sulphuric acid, the selenium itself. From the mercurial precipitate the selenium can be obtained by oxidizing with nitric acid, evaporating, neutralizing with sodium carbonate, fluxing with potassium nitrate, boiling with hydrochloric acid in order to reduce SeO_2 to SeO_3 , and precipitating the selenium from the solution by SO_2 .

Liebe (Wagner's Jahresb. 1860, p. 178) extracts the oxidized mass, after evaporation with sulphuric acid, with water, neutralizes with soda-ash, evaporates to dryness, mixes the residue with an equal weight of sal-ammoniac, calcines the mass in a porcelain dish (when the sal-ammoniac reduces the SeO_3), and washes with water, pure selenium remaining behind.

Böttger (Dingl. Journ. clxxvi. p. 405) extracts the selenium from the chamber-deposit washed with water by means of a concentrated solution of neutral sodium sulphite, and filters it into dilute muriatic acid, which at once precipitates the selenium.

Nilson (Ber. d. deutsch. chem. Ges. vii. p. 1719) describes the working-up of the Fahlun chamber-deposit for selenium. This cannot well be done by Otto's process; it is better to employ potassium cyanide, 2 parts of which yield 1 part of selenium. The washed deposit needs only to be digested with a concentrated

solution of potassium cyanide at 80° to 100°C . till its red colour has just been turned into pure grey; the residue is washed with boiling water, filtered, and hydrochloric acid added to the solution; selenium at once precipitates in cherry-red flakes, as the liberated selenocyanic acid is almost instantaneously decomposed into selenium and hydrocyanic acid; the sulphur dissolved at the same time remains in solution as sulphocyanic acid. The selenium thus obtained contains only a little copper, iron, and perhaps traces of mercury; it is obtained quite pure by dissolving in nitric acid, evaporating to dryness in a water-bath, subliming the anhydride in a current of dry air, and treating its solution with sulphurous and hydrochloric acids.

Kienlen (Bull. Soc. Chem. [2] xxxiv. p. 440) showed that the selenium, being reduced by SO_2 in the Glover tower, is dissolved in the sulphuric acid, to which it sometimes imparts a blood-red colour. When diluting it with three times its bulk of water, the selenium is precipitated. Glover acid contains up to 17.3 millig., chamber-acid 22.3 millig. per kilog. If such sulphuric acid is employed for the manufacture of hydrochloric acid, the selenium is volatilized together with HCl and is deposited in the first receivers as a reddish mud containing 41 to 45 per cent. Se , whilst the hydrochloric acid holds up to 21.4 millig. Se per kilog. The selenium is extracted from the mud by chlorine, which forms selenious and selenic acid. When the red colour has been destroyed, the mass is filtered, the filtrate is boiled with hydrochloric acid, and the selenium precipitated by sodium sulphite.

Bornträger (Dingl. Journ. ccxlvii. p. 505) found in the red mud from Glover-tower acid (made from Rio Tinto pyrites) after washing and drying, 12.60 per cent. Se (with 76.30 PbSO_4 &c.). He obtains the selenium from it by heating it in fireclay retorts at a red heat, with exclusion of air, as a black metallic sublimate, which is freed from As_2O_3 and SeO_2 by washing with strong caustic soda.

Divers and Shimosé (Chem. News, No. 1256) found in sulphuric acid made from Japanese brimstone 0.37 grm. tellurium, and 0.15 grm. selenium per litre, and in the sediment from the same acid 10.5 per cent. selenium and 1.2 per cent. tellurium. Shimosé (*ibid.* No. 1260) further describes the process employed by him for separating selenium and tellurium, viz., neutralizing the sediment with sodium carbonate, removing the selenium by digesting with

concentrated solution of potassium cyanide at a gentle heat (at first cold), diluting the mixture with water, and heating nearly to boiling. The solution, containing the selenium, is treated with hydrochloric acid in order to separate the Se; on the other hand the sediment from which the cyanide solution has been decanted yields tellurium by a treatment with sulphuric acid and a little nitric acid, and passing H_2S through the solution obtained.

The Mansfeld Kupferschiefer Mining Company (Wagner's Jahresb. 1876, p. 297) in 1875 produced

Selenium	2.38 kil.,	value £18.
Flue-dust containing selenium	4½ „ „	£6 2s.

The extraction of Copper from Pyrites-cinders.

This manufacture cannot properly be regarded as a by-work done in sulphuric-acid making; with as much, if not with greater, right the latter might be considered a secondary branch of the extraction of copper, since in the cupreous ores the value of the copper mostly exceeds that of the sulphur contained in them; but if the value of the final products be counted, that of the sulphuric acid certainly mostly far outweighs that of the copper. Even in the large English works now-a-days the extraction of copper from the cinders is rarely done in the chemical factory itself; the former is concentrated in a few works erected in the centres of the chemical trade, which receive the burnt ore from a whole group of chemical works. One of the largest pyrites-mining companies, the Tharsis Sulphur- and Copper-extracting Company, supplies its ores to the consumers only on condition of returning the burnt ore to the copper-works belonging to the same Company. A similar establishment was founded at Duisburg by a number of Rhenish manufacturers, likewise based on the extraction of Spanish-pyrites cinders. Although the production of copper thus does not belong to the usual cycle of vitriol- and alkali-works, yet it is most intimately connected with it, especially in Great Britain; and a short description of that production does not seem out of place here.

The percentage of copper in the ores in question (comp. p. 30) is mostly so small, rarely above 4 per cent., that its extraction by smelting would not pay. This can only be made possible at the outset by carrying on the first necessary operation (the calcining or burning) in such a way that the calcining gas does not go away into the air, but is taken into lead chambers and

sulphuric acid made of it, which helps to pay for the ore. But something else is necessary in practice. The cinders from burning the ore are still too poor in copper to be smelted in the usual way. They might possibly be smelted to coarse metal, with a mixture of a little green pyrites, siliceous sand, and slags; and this coarse metal might be sent to copper-works for further treatment; but in that case only a portion of the copper would be obtained, and the expense would be barely covered. When the quantity of poor ore coming into the market became larger, this way of utilizing it was out of the question. Other drawbacks in smelting for coarse metal, as they were observed at Oker, will be mentioned below.

Accordingly, since 1865, the copper of poor ores is always extracted *in the wet way*. From immemorial times the pit-waters arising from weathered ore have been precipitated by metallic iron, and *cement copper* obtained in this way; but the processes for converting the copper purposely into such compounds that it becomes capable of being dissolved and precipitated, all date from a recent period. Exact descriptions of the former processes are found in Percy's 'Metallurgy,' more recent processes in Stölzel's 'Metallurgie,' i. p. 714, and in Hofmann's 'Bericht' of 1873, p. 885 (this article is from the pen of Professor Kerl). Most of the volumes of Wagner's 'Jahresberichte' contain the literature of this branch.

It is beyond the scope of this book to enter specially upon all the proposed or really carried-out processes for copper-extraction in the wet way; we must refer the reader to the authorities just mentioned, and we shall only describe that process which for a number of years has been exclusively employed for working up the cinders from vitriol-works, viz. the *roasting with salt*, followed by the *precipitation by means of iron*. It appears that the interesting process of lixiviating by means of ferrous chloride, originally proposed by Schaffner, but best known in the shape given to it by Sterry Hunt and Douglas, is not in use at vitriol-works or at the copper-works in immediate connection with these; we must therefore, in respect of this also, refer to the originals.

The first attempts in this way seem to be referable to Hunt (patent of Jan. 21, 1840), and especially to Longmaid (patents of Oct. 20, 1842, and Jan. 1, 1844). The latter exactly described the principles of the process, as it is carried out to-day, certainly with a view to making salt-cake and chlorine as the principal products; and he also worked it out on a large scale; so that he must be re-

garded as the founder of the wet extraction of copper. Certain small improvements were patented at different times—for instance, by Gossage on July 17th, 1850. We find much later, in 1856, the process started with a good deal of noise as a novel one, by Bechi, of Florence, and Haupt, of Freiberg, for working the ores at Capanne Vecchie (Wagner's *Jahresb.* 1858, p. 68). It is strange that, 16 years after Longmaid, such a distinguished metallurgist as Gruner could ascribe the success of Bechi's process less to the influence of the common salt than to the fine grinding. Bechi and Haupt's process was patented in England in the name of Hähner on March 7th, 1856; it differs from Longmaid's process merely by much greater complication, such as calcining three times instead of once, and has long since been given up. Schaffner (Wagner's *Jahresb.* 1862, p. 119; 1871, p. 139) improved the process in several respects; but it was carried out on a large scale chiefly in England, by Phillips, Henderson, Tennant, and others.

Spongy iron was first employed by Gossage; it was again patented by Aas in 1861, and again by G. Bischof in 1862.

The process now generally employed in England has been principally described by Clapham (*Chem. News*, xxiii. p. 26), Wedding and Ulrich (Wagner's *Jahresb.* 1872, p. 152), Gibb (*Chem. News*, xxxi. p. 165, and several publications of the Tyne Chemical Society), by myself (*Dingl. Journ.* cciv. p. 288, ccxiv. p. 466, ccxv. pp. 54 & 229, ccxix. p. 323); the process at Oker by Bräuning (*Preuss. Zeitschr. f. Berg-, Hütten- u. Salinenwesen*, 1877, p. 156). Several more recent descriptions, *e.g.* that by Egleston (*Fischer's Jahresb.* 1886, p. 170), contain nothing of any importance. A paper by Bode (*Dingl. Journ.* ccxxxi. pp. 254, 357, and 428) gives a very complete survey of all the previous ones. In the following description the above sources are used, along with notes taken by me at several copper-works.

The three most important ores employed in the English factories contain from 47 to 49 per cent. of sulphur, and the following quantities of copper and silver:—

	Copper. per cent.	Silver. ounce, troy, per ton.
Rio-Tinto.....	3·80	1·20
Tharsis.....	3·50	0·75
San-Domingo.....	3·70	0·75

(N.B.—An ounce troy is = 480 grains ; there are 32,666 ounces troy to the ton.)

The “ordinary copper-ores” at Oker generally consist of 60 per cent. iron-pyrites, 23 per cent. copper-pyrites, 6 blende, 2 galena, 9 gangue (complete analysis, p. 69).

The percentage of sulphur in the cinders as they are supplied by the acid-works varies extremely ; hardly ever falling below 2 per cent., it sometimes rises above 10 per cent. The latter, however, results from very bad work indeed ; but 4 to 5 per cent. is considered very fair work ; and as much is indeed required for the wet copper-extraction, the sulphur may even amount to $1\frac{1}{2}$ times as much as the copper, but no more. At Oker the cinders are delivered to the extracting works with 5 to 8 per cent. sulphur and 6 to 9 per cent. copper. If the pyrites arrives too well burnt from the acid-works, the copper-works add a little green pyrites in order to have sufficient sulphur for the first stage of their process.

The following analyses by Gibb show the composition of the pyrites-cinders as the copper-works receive them :—

	Rio-Tinto.	Tharsis.	San-Domingo.	Ytterœn (Norway).
* { Copper.....	1·65	1·50	1·55	1·01
* { Iron.....	3·64	3·23	3·76	3·33
* { Sulphur.....	3·53	3·15	3·62	3·10
Cupric oxide.....	2·75	2·56	2·70	·39
Zinc oxide.....	2·02	·55	·47	6·46
Lead oxide.....	·47	·70	·84	·06
Silver.....	·0037	·0023	·0023
Cobaltic oxide.....	·007	·032	·033
Bismuth oxide.....	·013	·010	·013
Calcium oxide.....	·20	·25	·23	2·30
Ferric oxide.....	77·40	77·00	78·15	68·06
Sulphuric acid.....	6·10	5·25	5·80	6·56
Arsenic acid.....	·24	·17	·25	·05
Insoluble residue.....	1·45	5·85	1·85	8·74
	99·46	100·25	99·31	100·06

* Calculated as Cu_2S and Fe_2S_3 .

Phillips states the following as the composition of cinders from San-Domingo ore :—

Sulphur.....	3.66
Arsenic.....	0.25
Iron	58.25 (= 83.0 Fe ₂ O ₃)
Copper	4.14
Zinc	0.37
Cobalt	trace
Lead	1.24
Lime	0.25
Insoluble	1.06
Moisture	3.85
Oxygen and loss	26.93

Wedding and Ulrich found in samples from Widnes (a) and Hebburn (b) :—

	Sulphur.		Copper.	
	a.	b.	a.	b.
Altogether	4.12	3.75	4.08	5.75
Of this soluble in water...	43 p. c.	37 p. c.	46 p. c.	26.1 p. c.
„ „ „ HCl ...	55	59	22.2	13.3
In the residue.....	2	4	31.8	60.6
	100	100	100	100

According to Hjelt the cinders from Spanish pyrites contain 0.19 per cent. arsenic.

The Oker cinders showed, on an average of a month's work :—

Copper (principally as CuO)	7.83 p. c.
Iron (principally as Fe ₂ O ₃)	40.53
Lead (as PbO)	2.09
Silver	0.008
Zinc (as ZnO)	1.95
Manganese (as Mn ₂ O ₄)	0.40
Sulphur	3.80
Sulphuric acid (corresp. to 3.8 S) ...	9.51
Alumina	4.43
Other gangue	11.65

The sulphur must be mostly in combination with iron, since unburnt crude ore could be seen as cores on breaking up the lumps. The sulphuric acid is partly combined with lime, partly with metals, probably, as may be inferred from the well-known processes of roasting, in the first line with CuO and ZnO , in the second line with FeO or Fe_2O_3 . From this the following would appear to be the most probable composition of the cinders :—

CuO	9.80 p. c.	
Fe_2O_3	53.14	(=37.2 Fe)
FeS_2	7.13	(= 3.8 S)
PbO	2.25	
Ag	0.008	
ZnO	2.43	
Mn_2O_4	0.57	
SO_3	9.51	
Al_2O_3	4.43	
Other gangue...	11.65	

100.918

These cinders were formerly utilized in small blast-furnaces 7 ft. high, the first smelting yielding a rich coarse metal (55 per cent.) and a little blister-copper. Higher furnaces could not be used, on account of the large percentage of Fe_2O_3 , which would have been partly reduced. The drawbacks of this smelting were the short duration of the furnace-lining (47 to 72 hours), and great loss of metal by the slag and the flue-dust. Therefore, instead of smelting them, the cinders have latterly been worked up by the wet process.

The cinders are first *finely ground*, either by crushing-rollers or by edge-runners, and at the same time mixed with a sufficient quantity of *sodium chloride*, usually in its cheapest form, viz. rock-salt. This addition, where the furnaces are worked by hand, varies from 10 to 20 per cent., on an average it is 15 per cent. But with the mechanical furnace to be described below, only $7\frac{1}{2}$ salt per cent. of burnt ore are required. The ground mixture is passed through a cylindrical sieve with 8 holes to the inch; the coarse particles are sent back to the mill, where they are ground down

completely, so that the mixture always remains the same. The whole being finely ground, it is filled into iron bogies and run on tramways over the calcining furnaces.

At Oker the cinders are mixed with 15 per cent. (formerly 20 per cent.) of Stassfurt potash salts (carhallite) and are ground down to the size of 2 millims. The Stassfurt salts contain the chlorides of magnesium, potassium, sodium, and calcium, all of which assist in the calcining process.

The *calcination* takes place in furnaces of very different kinds. These may be classed as follows:—

1. *Ordinary reverberatory furnaces*, similar to black-ash furnaces. These were in use at first, but have been given up long since.

Fig. 343.

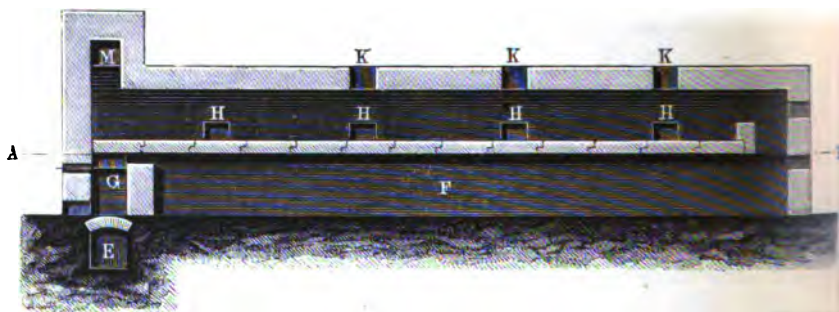
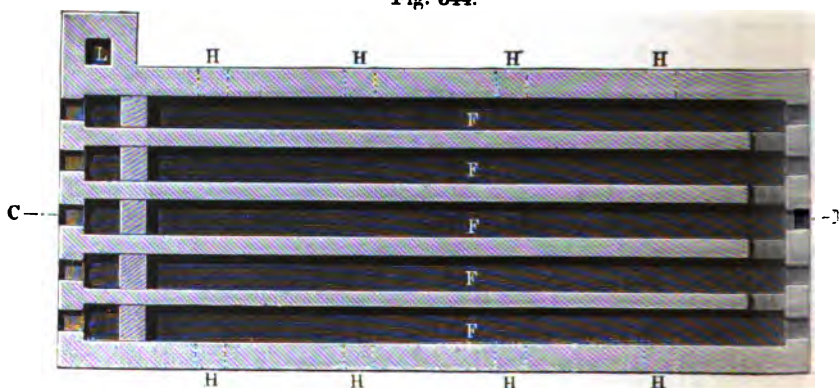


Fig. 344.

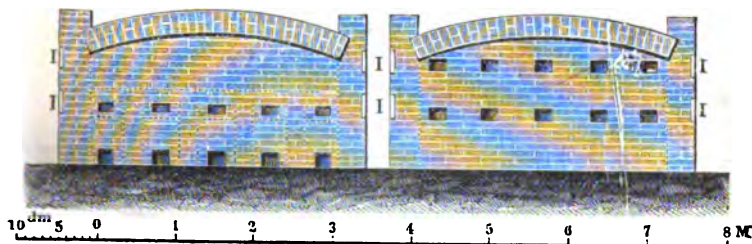


2. *Reverberatory furnaces with gaseous fuel.* These are principally used in Lancashire; they are illustrated by figs. 343 to 344.

Three gas-producers furnish the gas for eight calcining furnaces; it passes from the main flue into the flue E across the width of the furnace; from this it rises through 5 vertical flues G, each of them provided with a damper; it then travels through the flues F below the furnace-bed, then directly over the charge and through the outlet M to the condensers. The air for combustion is introduced by two tiers of holes with slides in each of the two furnace-ends (figs. 345 & 346), so that one of the tiers communicates with the

Fig. 345.

Fig. 346.



flues below the bed, the other with the space above the fire-bridge. Thus the combustion can be regulated so that some unburnt gas gets as far as the fire-bridge and is only lighted there. H H are the working-doors; K, charging-holes in the arch, closed by loose metal plates and fine ore on the top of these; I, binding-plates. Each furnace holds 45 cwt. of ore.

Similar furnaces are used at Oker; these are represented in figs. 347 to 350. They work two charges of $2\frac{1}{2}$ tons each every 24 hours. Here *f* marks the main channel for the gas; *g g*, 5 channels for the same below the furnace-beds; *h*, the slits for introducing the air; *i*, the outlet for the mixed fire- and calcining-gas to the condenser; *l*, the working-holes; *m*, the charging-hopper.

Fig. 347.

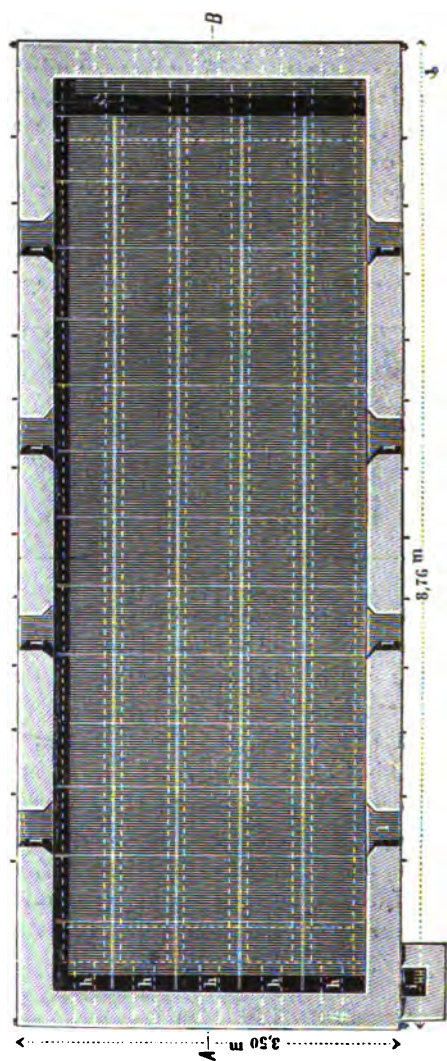


Fig. 348.

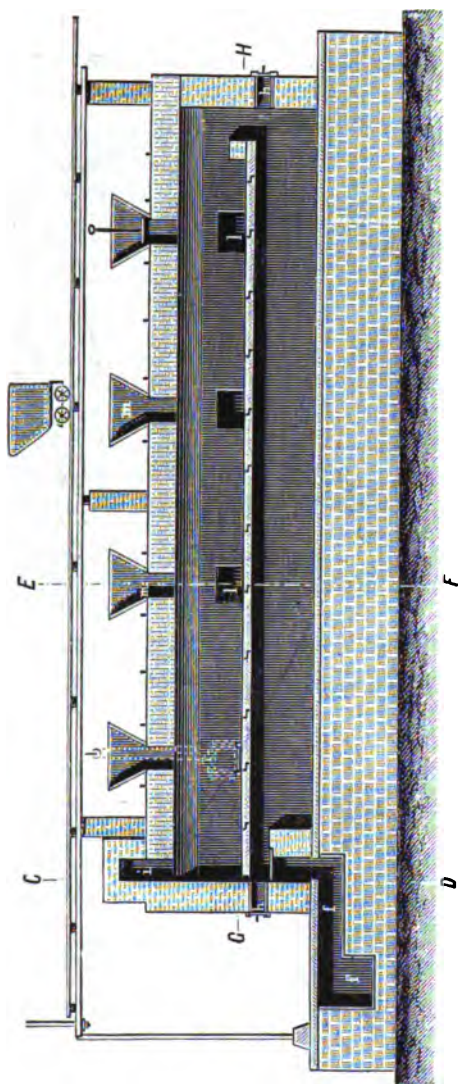
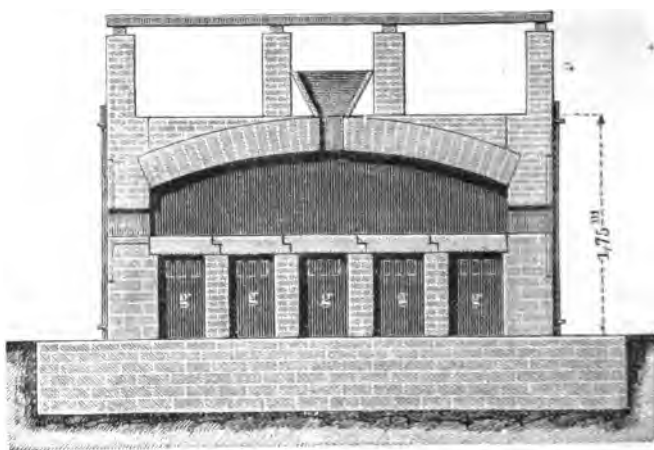


Fig. 349.



Fig. 350.



3. *Blind roasters* (muffles), employed at all the works of the Tharsis Sulphur and Copper Co., figs. 351 to 353. Here the flame

Fig. 351.

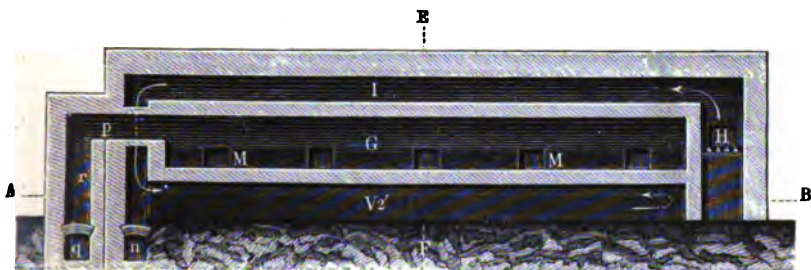


Fig. 352.

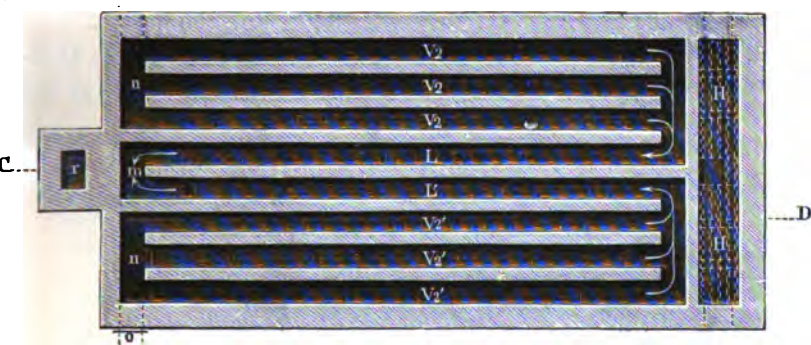
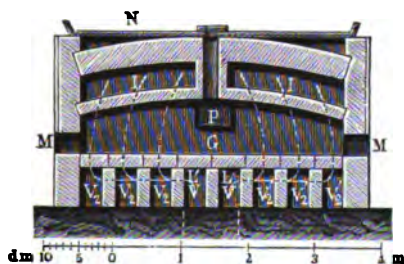


Fig. 353.



does not come into direct contact with the charge, but only acts through the brickwork of the bed and the arch. The charge is worked in the muffle G, with the working- and discharging-doors

M. Its bottom is formed by fire-clay slabs covering the fire-flues V L; its cover by a thin arch. The ore is spread in a thin layer, and receives the air necessary for its roasting only through the working-doors M; in the other part of the furnace the oxygen contained in the fire-gas is active as well. The flame from the double grate H first travels by I over the muffle-arch, then downwards in three channels on each side (V_2 & V'_2). The gas of each three channels is united in a flue (L & L'), and, after having returned in the opposite direction, descends by m into the flue n situated below the ground-line, which enters the main chimney. o is the regulating damper; p , the outlet for the calcining-gas, which descends by r to the horizontal subterraneous flue q , and thence arrives at the acid-condensers. The metal dish N, on the top of the furnace, serves for a first heating of the mixture; it communicates with the muffle through several pipes, usually covered with a metal plate; by raising the latter the mixture is let down into the muffle.

4. *Combined furnaces*, used by the Bede Metal Company at Hebburn-on-Tyne (shown in figs. 354 to 357). Here the flame of the

Fig. 354.

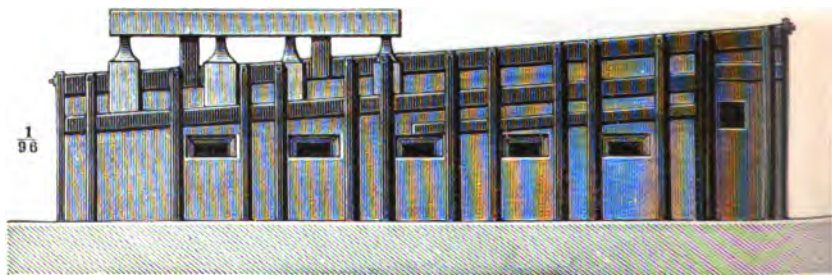


Fig. 355.



Fig. 356.

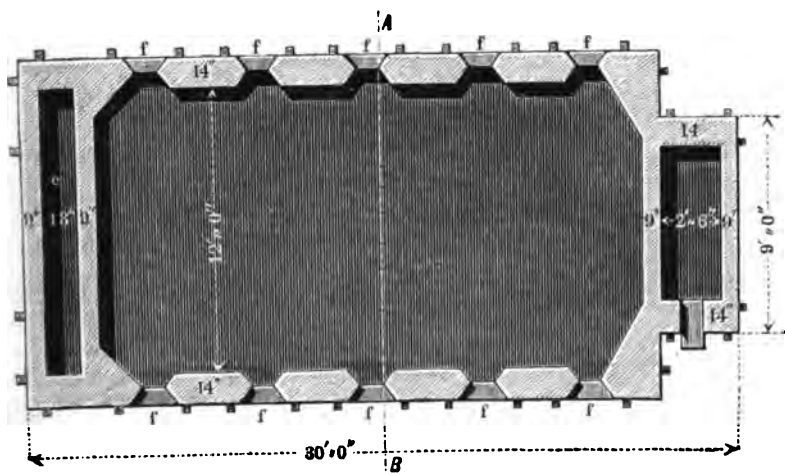
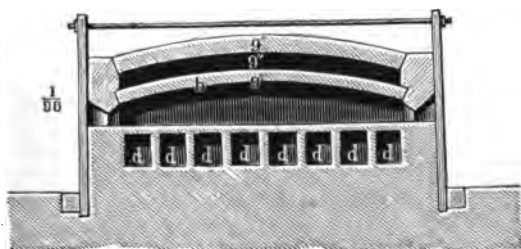


Fig. 357.



fire, *a*, does not play direct upon the charge, but is kept off it by an arch, *b*, reaching half the length of the furnace; after this the flame touches the furnace-bed directly and descends by *c* in order to return by 8 channels, *d d*, beneath the furnace-bed, and to escape at *e* into an underground flue leading to an acid-condenser. The working-doors *ff* serve for stirring and discharging; the pan *g* for a first heating of the charge; the pipes *h h* for dropping it into the furnace. The purpose of the arch *b* is to avoid overheating those portions of the ore nearest the fire-bridge, in which the copper might easily be roasted dead; in fact the hottest part of these furnaces is that behind, the part below the protecting arch hardly attaining a dark-red heat.

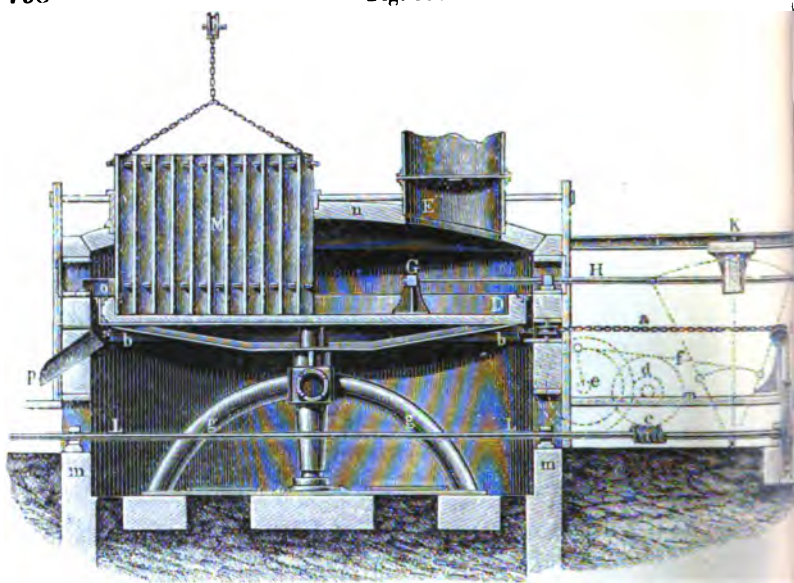


Fig. 359.

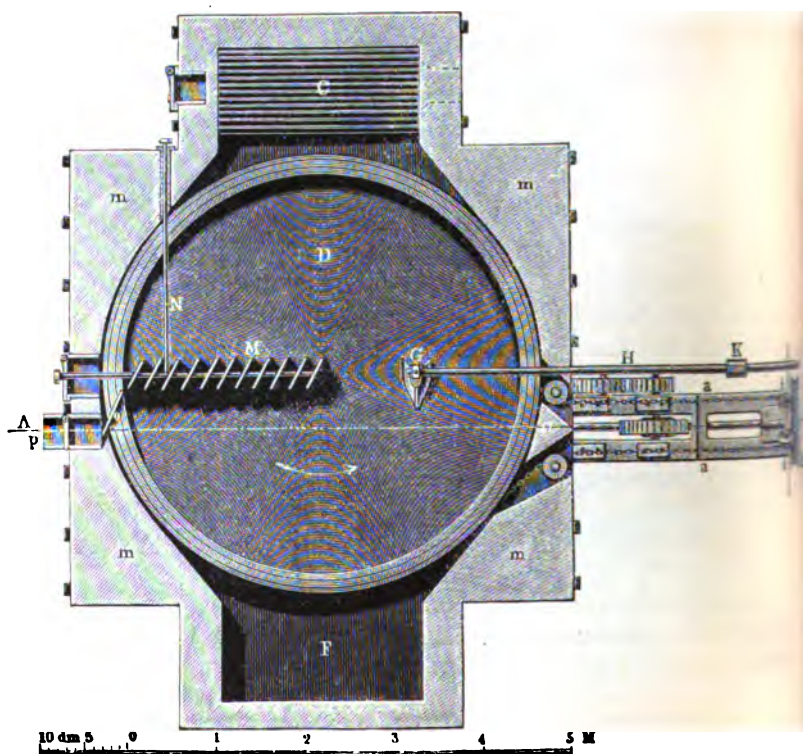


Fig 360.

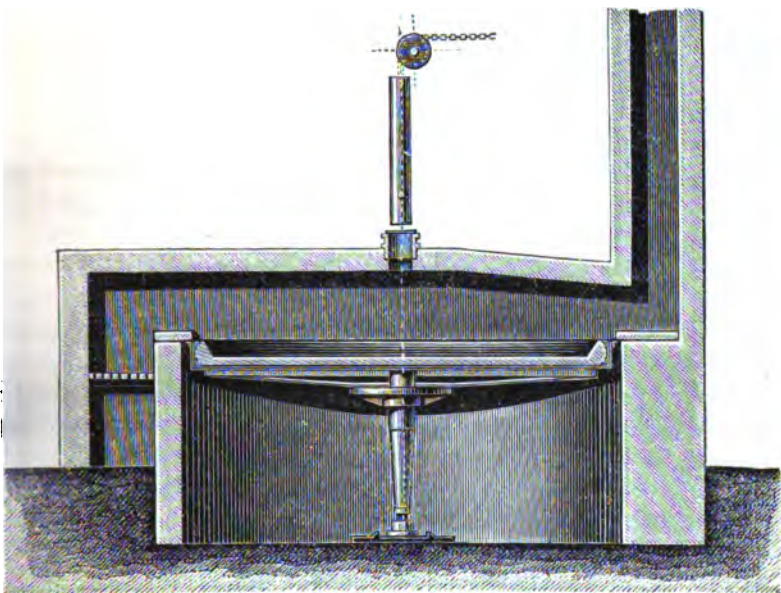
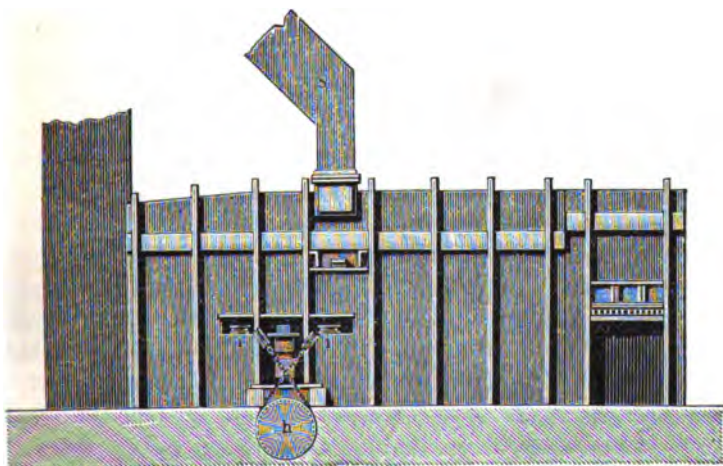


Fig. 361.



5. *Mechanical calcining-furnaces with revolving hearth*, patented in 1872 by Gibb and Gelstharpe, and 12 of which exist at the Bede metal-works. Figs. 358 to 361 represent this furnace. The bed

consists of a circular pan, *b b*, made of boiler-plate, lined with fire-bricks, *D*. The side walls (*m m*), and the arch (*n*) form the other parts of the calcining-space. On one side there is a fire-place, *C*, whose flame travels across the hearth to *F*, whence it enters an underground flue leading to the chimney, along with the gas evolved in calcining. The pan *b b* is carried on wrought-iron girders fixed on a central cast-iron spindle which works in a footstep and is maintained in a vertical position by a collar, fitted with brasses, in which an upper bearing of the spindle works, carried by the tubular cast-iron stays *g g*. This pan is caused to revolve in its own plane on the central footstep by an endless chain, *a*, carried round a sheave, *I*, from which it passes over the guiding-pulleys *i i* to the horizontal sheave underneath the pan.

A small pump, driven by the same main shaft, constantly pumps lubricating oil from a tin vessel into the footstep, the excess of oil running back into the same vessel again. The hearth is traversed by a cast-iron plough, *G*, made to reciprocate in a radial line of the circle by the wrought-iron arm *H* connected with the cross head *K*. The motion of this cross head is equal to the radius of the hearth, and is derived from the driving-shaft *L* by means of the worm and scroll-wheel *c* and the pair of spur-wheels *d* and *e*, the larger of which, by means of the crank-pin and connecting-rod *f*, gives a reciprocating motion to a lever, the forked upper end of which, by means of pins working in slots, moves the cross head with the plough-arm and plough. The speeds of the circular hearth and the plough are so adjusted that the plough does not travel more than its own breadth during one revolution of the hearth; so that every part of the circle of the hearth is gone over by the plough in each journey from or to its centre.

The furnace is charged by means of the hopper *E*, let into a slit of the arch, and discharged by a set of parallel plates *M*, which are arranged obliquely across a radial line of the circle of the hearth on the opposite side of the centre to that in which the plough travels. These plates are rigidly bound together at top and bottom, and suspended by a chain, so that they can be raised out of or lowered into the furnace through the roof. The plates are shown in the furnace in the position for discharging, with a plate, *o*, fixed in the doorway, folded against the outer plate of the series *M*. When the discharging-plates are in this position, each throws the ore carried against it by the revolution of the hearth towards

the circumference into the path of the next outward plate, by which it is again thrown outwards at the next revolution, to be at length propelled against the doorway-plate *o*, which throws it from the edge of the hearth on a shoot, *p*, over which it runs on to the floor outside the furnace. When the furnace is working, the plates are raised through the roof, and the opening through which they pass is closed by a slide. The bolt *N* fixes the plates in their position.

In order that the pan may freely revolve round the spindle, the side walls *m m* are 1 inch apart from the edge of the pan; the air rising in this intermediate space causes the oxidation. The brick-work reaches down to the ground-line; and the machinery underneath the hearth is only accessible by an iron door, so that it is protected from the coal- and ore-dust. Every part of the machinery is very strong, and not liable to get out of repair—excepting the cast-iron plough, *G*, which must be replaced once a fortnight, but at a smaller expense than that of the tools in a furnace worked by hand. The plates *M* suffer very little, because they are only for a very short time exposed to the fire. The twelve furnaces at the Bede metal-works are driven by two steam-engines of 18 indicated horse-powers each.

All these different descriptions of furnaces have the same object; and the *style of working* is accordingly very similar in all cases. The ore must, of course, be completely roasted—that is, sufficiently to convert the copper into sulphate, which, owing to the presence of sodium chloride, at once forms with this, by mutual decomposition, cupric chloride and sodium sulphate; whilst the iron should be converted as completely as possible into ferric oxide, so as to become insoluble. In this process, owing to the simultaneous action of SO_2 and O upon NaCl , chlorine is evolved, which must greatly aid in chlorinating the copper as well as any other metal present. At the same time a large quantity of HCl is formed, which converts the oxides of copper, silver, zinc, &c. into chlorides, whilst at the calcining-temperature ferric chloride cannot continue to exist as such. At Oker the formation of hydrochloric acid is purposely aided by using carnallite in lieu of common salt, as the MgCl_2 contained in the former readily yields MgO and HCl . This, however, is not absolutely requisite, as with 2NaCl the CuSO_4 already produced in calcining yields CuCl_2 and Na_2SO_4 . Cu_2Cl_2 also is always formed at the same time. Since the chlorides of copper are both unstable

and volatile at very high temperatures, a low red heat ought not to be exceeded; so that any copper-pyrites still present in the cinders is not burnt, and therefore escapes chlorination. Accordingly, copper-pyrites (or Cu_2S) ought not to be present in any quantity for the wet-extraction process; and consequently ores with more than 8 per cent. of copper, which can never be roasted with sufficient completeness in the chemical factories, cannot be utilized by this process, but only by smelting.

Manifold experience has taught that without employing common salt (that is, without chlorinating) it is never possible, even approximately, to hit the point where the more easily decomposed ferric sulphate no longer exists, whilst the less easily decomposable cupric sulphate is still present as such, the iron being then present in an insoluble, the copper in a soluble form. If ferric salt remains in a soluble form, it naturally passes over into the lyes, and, in the operation of precipitating the copper, causes a great loss of metallic iron by its reduction to ferrous salts. If, on the other hand, much copper has likewise passed into an insoluble form, more hydrochloric acid is required for its solution. In any case the formation of some cupric oxide and cuprous chloride, insoluble in water, cannot be avoided.

Wedding has observed, and described in detail, the calcining process as carried on at Widnes in a gas-furnace. The charge, of 45 cwt. of ore mixed with 17 per cent. of salt, is let down on to the hearth, spread out and slowly heated till a low red-heat has been reached nearest the fire-bridge; the charge is turned over and left to itself, the gas being shut off, but the air being allowed to enter, so that after two hours scarcely any glowing can be perceived at the fire-bridge. After one hour's and three hours' calcining respectively, the copper of the charge behaved as follows:—

	1 hour's calcining. per cent.	3 hours' calcining. per cent.
Soluble in water.....	54	51
„ HCl	38	42
„ NO_3H	8	7

After three hours the charge is quite dark, and is now well turned over with a slice of 3 or 4 inches breadth, as well as with a rake; there ought to be no necessity for giving more fire, as the temperature should from the first have been raised to the proper

point. On raking over the charge, which is now done regularly with short interruptions only, the temperature rises of itself in consequence of the chemical reactions, the rise becoming sensible after $4\frac{3}{4}$ hours (counting from the beginning); so that after $5\frac{1}{4}$ hours a dark-red heat has been reached. Up to this point there is a copious evolution of white vapours and blue flames; from this period there is less of these, and it is the calciner's principal task to see that the heating of the charge is quite equal all over, and that some places do not show more blue flames than others. After $6\frac{1}{2}$ hours these flames are almost entirely gone; and this fact, along with the greenish-grey colour of the charge, are the practical tests for judging whether the operation is finished. A sample is now drawn; and if its examination shows the completion of the calcining-process, the charge, which has now been $6\frac{1}{2}$ or $6\frac{3}{4}$ hours in the furnace, is drawn out. Of the copper now

75	per cent.	is soluble in water,	
20	"	"	HCl,
5	"	"	NO ₃ H.

Good workmen can finish the calcining in a gas-furnace in six hours.

Wedding observes that the watery solutions constantly show more sulphur, and that the testing of the calcined ore of different works proves the process to be carried out very unequally; but it is certain that the best results are in fact got by the most careful work. The calciner's task is, first to heat the charge and thus to start the chemical reactions, but then to maintain these at the lowest possible heat up to the finish, and to spread them equally through the whole mass. It is of great importance not to leave the ore any longer in the furnace than exactly the necessary time; this is made difficult by the depth of the layer of ore, viz. 5 or 6 inches—which, on the other hand, facilitates the chlorination, since the gas rising in the ore heated both at top and bottom has all the more opportunity of coming into contact with all parts of it.

Evidently the process is altogether dependent upon the skill of the workman, whilst with the mechanical furnace of Gibb and Gelstharpe only the firing needs attention. In the latter furnace indeed a lower heat is sufficient, one that never reaches a red glow visible in daylight.

At Oker, where gas-furnaces exactly like those at Widnes are used, each charge of 50 cwt. of ore with 15 per cent. potash salts is

brought to a low red heat in four hours; the firing is then interrupted and the mass raked over. Owing to the chemical reactions, the heat at first increases, but towards the end goes back again. During the turning-over stage, which lasts five hours, the air-slides are opened to admit the air to the charge; after that time the charge is drawn. Two charges are put in every 24 hours. Analysis of a sample taken in the middle of the calcining-process (the mixture containing 20 per cent. carnallite) :—

<i>Soluble in water.</i>				<i>Insoluble in water.</i>			
	per cent.		per cent.		per cent.		per cent.
Cu	1.94, calc. as CuCl ₂	3.11	Cu	4.32, calc. as	{ CuO sol. in HCl	5.12
Ag	0.003, "	AgCl	0.004			{ Cu ₂ S sol. in aqua regia	0.29
Fe	0.74, "	FeCl ₂	1.68				
Al ₂ O ₃	0.11, "	Al ₂ (SO ₄) ₃	0.39	Pb	0.39, "	PbSO ₄	0.57
Mn	0.69, "	MnCl ₂	1.58	Fe	34.49, "	{ Fe ₂ O ₃	45.36
Ni	0.20, "	NiCl ₂	0.44			{ Fe ₂ (SO ₄) ₃	3.27
Zn	1.60, "	ZnCl ₂	3.40			{ FeS ₂	2.64
CaO	2.76, "	CaCl ₂	6.27	Al ₂ O ₃	3.30, "	Al ₂ O ₃	3.30
MgO	}	Sulphates	18.15	Mn	0.03, "	Mn ₂ O ₃	0.04
K ₂ O				Zn + Ni	0.29, "	ZnO + NiO	0.36
Na ₂ O				CaO	0.45, "	CaSO ₄	1.09
				SO ₂	1.86		
				S	1.47		
				Cl	trace.		
				Insoluble in acids			2.96
			35.024				65.02

Sample of calcined ore taken at the finish :—

<i>Soluble in water.</i>				<i>Insoluble in water.</i>			
	per cent.		per cent.		per cent.		per cent.
Cu	3.86, calc. as CuCl ₂	8.17	Cu	2.57, calc. as	{ CuO	3.18
Ag	0.005, "	AgCl	0.006			{ Cu ₂ S	0.03
Fe	0.60, "	FeCl ₂	1.38				
Al ₂ O ₃	0.17, "	Al ₂ (SO ₄) ₃	0.56	Pb	1.17, "	PbSO ₄	1.26
Zn	1.64, "	ZnCl ₂	3.42	Fe	34.56, "	{ Fe ₂ O ₃	47.91
Mn	0.75, "	MnCl ₂	1.71			{ Fe ₂ (SO ₄) ₃	1.72
Ni	0.07, "	NiCl ₂	0.15			{ FeS ₂	1.15
CaO	1.60, "	CaCl ₂	3.17	Al ₂ O ₃	0.44, "	Al ₂ O ₃	0.44
MgO	}	Sulphates	20.50	Zn	0.37, "	ZnO	0.46
K ₂ O				Mn + Ni	trace.		
Na ₂ O				CaO	0.49, "	CaSO ₄	1.19
				SO ₂	1.49		
				Cl	trace.		
				S	0.64		
				Insoluble in acids			3.79
			39.066				60.36

The mechanical furnace has the advantage also in respect of the addition of salt; only $7\frac{1}{2}$ per cent. of salt is required in it, against 15 in the hand-furnaces. Often only a portion of the salt is mixed with the ore at the outset, and the remainder added afterwards. In the blind roasters the ore is calcined first nine hours with 12 per cent. salt, and another three hours with 8 per cent. more salt. In the combined furnaces with protecting arch the weight of ore is 58 cwt., and the time of calcining eight hours; in the mechanical furnaces 5 tons and nine hours.

Gibb gives the following analyses of the results of calcination:—

	Gas-furnace.	Oleose furnace.	Mechanical furnace.
	p. c. Cu p. c.	p. c. Cu p. c.	p. c. Cu p. c.
Cupric chloride ...	4.03 = 1.90	4.25 = 2.00	6.70 = 3.15
Cuprous chloride32 = .20	.35 = .21	nil.
Cupric oxide.....	1.26 = 1.00	.88 = .70	.32 = .25
Sodium chloride ...	2.50	3.40	0.90
Sodium sulphate ...	13.18	17.40	14.03
Insoluble copper15	.12	.13
Total copper.....	3.25	3.03	3.53

The principal point is always this, that as little copper as possible should remain in a state insoluble in water and dilute acids. In the above cases the quantity varies from 0.12 to 0.15 per cent.; the slightly more favourable result of the blind roaster, according to Gibb, is far more than counterbalanced by its greater consumption of fuel (50–100 per cent.). The most favourable result is obtained with the mechanical furnace, in which next to no cuprous chloride and, even with the worst ores, rarely more than 0.25 per cent. of CuO are formed.

At Oker the average result of the constantly taken samples of calcined ore in this: 75 per cent. of the copper contained in the ore is soluble in water, 20 per cent. in dilute muriatic acid, and 5 per cent. in aqua regia.

If the pyrites contains more than 4 per cent. copper, the cinders

in England cannot be worked with advantage by the wet process. At the Bede metal-works many experiments have been made with richer ores; but with 6 per cent. copper the salt, the coals, and the labour are already too dear. In this case, however, another circumstance comes into play: by the Cornish copper assay about 2 per cent. copper less than the truth is indicated; and this with a poor ore of course amounts to a much larger proportion of the whole (sometimes more than half) than with richer ores; thus the former are cheaper for the wet process than the latter. In the Harz, where this reason does not exist, ore up to 8 per cent. Cu can be extracted by the wet process.

It has already been remarked that the sulphur in the cinders must bear a certain proportion to the copper; with a 4-per-cent. ore it ought not to exceed 6 per cent.; an equal percentage of S and Cu is preferable. If less S is present, raw pyrites must be added. The more S there is present, the more salt must be added, and the more time will the calcination take.

The *tests* for ascertaining the completion of the calcination are of a very simple character, which is the more necessary as they must be made very quickly. A certain *measure* of the charge, not weighed, is lixiviated by water and dilute HCl, just as on the large scale; the residue is boiled with aqua regia, supersaturated with ammonia, and allowed to settle; the more or less blue colour of the solution of ammonio-cupric salt gives a sufficient indication of the percentage of insoluble copper.

Condensation of the calcination-gas.—In all the descriptions of furnaces mentioned above, except the blind roasters, this gas is mixed with the fire-gas, but even in these it is mixed with air to such an extent that a condensation of strong acid is not very well possible. The acid is a little more concentrated than that from open calciners; but this matters very little, as it is always used in a very dilute state for lixivating. The calcination-gas principally contains (besides oxygen and nitrogen) SO_2 , SO_3 , HCl, Cl, and very small quantities of metallic chlorides. Henderson had proposed to volatilize the copper entirely as CuCl_2 , and condense the latter in towers; but this has turned out quite impracticable. The small quantity of copper passing over into the condensers, about $\frac{1}{4}$ per cent. of the whole, is not lost, as the condensed acid is used for lixiviating the charge.

The condensation of the gas from the calciners takes place in towers of exactly the same kind as those (described in detail in the second volume) for muriatic acid—that is to say, made of brick-work set in tar and sand (or, better, of stone flags), and packed with coke, fire-bricks, and the like. Sometimes condensers made of very large stoneware pipes are employed. Coke can be used with blind roasters; but the other furnaces require bricks &c., and must have larger condensers, as these have to serve for a larger volume of gas. The size of the towers varies with that of the plant; for 12 furnaces a tower of 8 feet square and 40 to 50 feet high is sufficient. The gas enters at the bottom, meets a spray of water coming from the top, which washes the acids out of it, and again leaves the tower at the top, whence it is taken downwards into a flue leading into the chimney.

The total condensed liquid (a mixture of weak sulphuric and muriatic acids; the SO_2 in the condensation is oxidized to SO_4H_2 by the action of the chlorine) is used in the succeeding operation of lixiviating, and frequently is not even sufficient for dissolving all the CuO and Cu_2Cl_2 .

Lixiviation of the calcined mixture.—The mixture is carried in bogies running on tramways over each of the lixiviating tanks, and tipped into these. The only available material for the tanks is wood; most metals are excluded by the nature of the lixiviating liquid; stone, asphalt &c., both by their costliness and by the heat of the charge. As such large wooden vessels cannot well be kept tight, on account of the unavoidably rough treatment and the hot acid liquors, the whole floor of the lixiviating shed is covered with a thick layer of asphalt and slopes to one side, so that all liquors leaking out run off to a catch-well, into which enter at the same time earthenware spouts for carrying the strong copper-liquors.

The lixiviating tanks are square, about 11×11 feet wide and 4 to 5 feet deep, made of well-seasoned and planed 3-inch planks, kept together by corner-pieces, screw-bolts, &c. The joints are tightened by putting on a little red lead before putting the planks together; the bottom joints are besides caulked with tarred spun yarn, and the whole vessel painted with hot coal-tar. At Oker lead-lined vessels are used, which are very expensive and frequently needing repair. On the bottom, laths on end are placed; upon these,

perforated fire-tiles or boards ; upon this false bottom a layer of sifted furnace-cinders is spread out ; and on the top a layer of heather or coke (at Oker of straw) 3 to 6 inches deep is put. The liquors are conveyed in earthenware and india-rubber tubes of 3 to 4 inches diameter, the latter provided with iron pinch-clamps. In order to force the liquors from one tank to the other, or from the catch-well into the tanks, simple stoneware injectors are provided. Each tank has a steam-pipe for heating.

Into each tank about 10 tons of calcined ore are put, quite hot from the furnaces, and are first covered with weak liquor from a previous operation, which gets heated by the heat of the mass itself. After one or two hours the now concentrated liquor is run off by a plug-hole below the false bottom, and goes forward to the precipitation. The plug is put in again, and the lixiviation continued by hot water ; thus weaker liquors are produced, which are forced to a fresh tank as just described. Generally three waters are put on, and thus most of the purest copper and 95 per cent. of all the silver contained in the pyrites are obtained. Then follow several (up to 6) washings with the weak condenser-acid, or, if this does not suffice, with muriatic acid bought for the purpose and much diluted. This is not necessary with mechanical furnaces, because the copper-salts from these are mostly soluble in water ; but it is generally necessary with hand furnaces. Even when no acid need be bought, but sufficient condenser-acid is obtainable, a saving of acid is important, since the condenser-acid conveys arsenic and bismuth into the copper.

The liquors obtained by the use of acid contain many impurities, especially As, Bi, Sb, and Pb—according to Gibb, for each 100 parts of Cu, 5·4 As and 0·3 Bi ; and they are accordingly treated separately in most works, because they yield impure copper.

It is a principal rule to allow each water only to stand a few hours on the ore ; the nine washings of each tank, together with charging and emptying it, are not to last beyond 48 hours. Accordingly, for each 5 tons of calcined ore obtained per diem one tank is required, and besides, on the whole, a few reserve tanks.

The residue from lixiviation, after draining, is tipped on a heap and afterwards sold to the iron-smelters. Just the value of this residue makes the wet process in this case more profitable than the dry process, as it forms a valuable iron-ore, going by the name of

“purple ore” or “blue billy.” The following is the composition of two average samples :—

Ferric oxide.....	90·61	95·10
Copper.....	0·15	0·18
Sulphur	0·08	0·07
Phosphorus	0	—
Lead sulphate	1·46	1·29
Calcium sulphate.....	0·37	0·49
Sodium sulphate	0·37	0·29
Sodium chloride	0·28	—
Insoluble	6·30	2·13
	—	—
	99·62	99·55
Metallic iron	63·42	66·57

This ore is thus shown to be very rich in iron, entirely free from phosphorus, and to contain very little sulphur : its slight percentage of copper does no harm. The only drawback is its fine state of division. Attempts have been made, but unsuccessfully, to conglomerate it by means of lime for use in blast-furnaces (see above, p. 774); but success has been obtained when employing it directly in its pulverulent state as a mixture with 5 or even only 3 parts of lump iron-ore ; using limestone in addition, both grey and white pig can be made from it. Most of this ore, however, is used for “fettling” the sides and bottom of puddling-furnaces in lieu of hæmatite, for which it is very well adapted. Its direct conversion into iron and steel on the large scale has not yet been carried out ; but experiments in this direction made in America with the Du-Puy process (‘Chemical News,’ xxxix. p. 36) have been very successful. At Oker it is easily used up in the various metallurgical processes there carried on, and even its small percentage of copper is turned to account. They obtain, upon 100 parts of pyrites-cinders, 75 parts of extraction residues of the following composition :—

Ferric oxide	79 per cent.
Alumina	3 „
Magnesia and alkalies	1 „
Lime	2·5 „
Sulphuric acid	5·5 „
Insoluble in acids	6 „

Purple ore is more valued the freer it is from siliceous gangue; and for this reason that made from Spanish and Portuguese is preferred to that from Norwegian pyrites.

The *lead* contained in the pyrites remains behind in the lixiviated residue in the shape of sulphate, mixed with the purple ore and injuring its quality as an iron-ore. Schaffner (Fischer's Jahresb. 1880, p. 136) removes and utilizes the lead in the following simple and cheap manner. After roasting the ore with common salt as usual and washing out all soluble chlorides and sulphates, the residue is drenched with chloride-of-calcium liquor (from the Weldon chlorine process) of 9° – 12° Tw., heated to about 40° C., and acidulated with hydrochloric acid. By mutual decomposition gypsum and lead chloride are at once formed, which remain *dissolved* in the acid liquor. This is run off and brought into contact with metallic iron, which precipitates the lead in the metallic state. After washing, the purple ore is quite free from lead sulphate. At the same time the CaCl_2 dissolves the last traces of copper and silver present as Cu_2Cl_2 and AgCl ; these are precipitated along with the lead. It should be noticed that sulphuretted hydrogen fails to indicate the lead in a solution of PbCl_2 in CaCl_2 acidulated with HCl .

Where the copper is precipitated by spongy iron, a portion of the purple ore is employed for preparing the latter.

The effect of the lixiviation is best seen from the following analyses by Gibb, which at the same time illustrate the great difference of work between mechanical and hand-worked furnaces:—

	Mechanical-Furnace Ore.		Hand-worked-Furnace Ore.	
	Copper,		Copper,	
<i>Soluble in Water:—</i>	per cent.	per cent.	per cent.	per cent.
Cupric chloride	4.16	1.96	3.81	1.82
Cuprous chloride	none		.19	.12
Cupric sulphate	1.83	.81	none	
Ferrous sulphate15		none	
Ferric sulphate75		none	
Zinc sulphate	2.01		1.95	
Calcium sulphate	1.29		1.39	
Sodium sulphate	9.17		11.13	
Sodium chloride	none		2.64	
Carried forward	19.36	2.77	21.11	1.94

Brought forward	19.36	2.77	21.11	1.94
<i>Soluble in dilute Hydrochloric Acid:—</i>				
Cuprous chloride015	.01	.33	.21
Cupric oxide225	.18	1.01	.81
Lead sulphate.....	} not determined.	}	not determined.	}
Ferric oxide				
<i>Residue (by difference):—</i>				
“purple iron-ore”.....	80.40	.08	77.55	.11
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	3.04	100.00	3.07
Sodium chloride equivalent to sodium				
salts as above.....	7.56		11.81	

The composition of the copper-liquor, according to Gibb, is, in grams per litre :—

From hand-work Furnaces.		From mechanical Furnaces.	
Sodium sulphate.....	144.1	Sodium sulphate.....	110.9
Sodium chloride.....	63.9	Sodium chloride	4.1
Chlorine in combination with heavy metals	87.1		
Copper.....	53.0	{ Cuprous chloride	53.2
Zinc	6.9	{ Cupric chloride	0.8
Lead	0.6	Zinc sulphate	10.1
Iron	0.5	Lead sulphate.....	0.8
Calcium	0.7	Ferrous sulphate	4.3
Silver	0.047	Calcium sulphate	5.0
		Silver.....	not estimated.

At Oker the process is carried out in the following way. The calcined charge is lixiviated in parcels of 5 tons each, first with the “final liquor,” which is always regenerated in the process. 100 parts of the latter, of 1.145 spec. grav., contained :—

	per cent.		per cent.
Cu	0.015	CoO + NiO...	0.01
Pb	trace	CaO	0.12
FeO	2.14	MgO	0.52
Fe ₂ O ₃	0.15	Alkalies	2.61
Al ₂ O ₃	0.11	Cl	2.56
ZnO	0.06	SO ₃	5.89
MnO	0.31	As + Sb	trace

Total solids..... 14.495 per cent.

This liquor, already heated in pumping by the injector to 50° C., is further heated, when it comes into contact with the calcined charge,

by the solution of the anhydrous salts, of course also by the heat of the charge itself, nearly up to the boiling-point, by which the solution is assisted. When the charge is perfectly penetrated by the final liquor, the outlet-tap is opened and fresh final liquor runs in as long as the copper-liquor running away at the bottom still shows a blue colour. This first period lasts four or five hours, and furnishes a copper-liquor of 1.355 spec. grav., and of the following composition :—

	per cent.		per cent.
Cu	3.71	CoO + NiO...	0.04
Pb	0.01	CaO	trace
Ag	0.005	MgO	0.27
Bi	trace	Alkalies	10.60
Fe ₃ O ₃ + Al ₂ O ₃ .	0.29	Cl	12.56
ZnO	4.97	SO ₃	8.95
MnO	0.58	As + Sb	0.32
Total solids.....		42.305 per cent.	

After the first lixiviation is over, the dilute condenser-acid, first brought to boiling, is run into the tanks and allowed to act for twenty-four hours; then it is run off, and a third lixiviation effected by dilute sulphuric acid. For 5 tons of ore 2½ cwt. of chamber-acid of 106° Tw., diluted to 12° Tw. and heated to the boiling-point, is employed, and allowed to remain in contact with the ore for two days, or until the liquor acquires a neutral reaction. Its analysis showed :—

	per cent.		per cent.
Cu	0.58	CaO	0.07
Al ₂ O ₃ + Fe ₂ O ₃ .	2.13	MgO	0.04
ZnO	0.06	Alkalies	0.62
MnO	0.12	Cl	0.13
Co + Ni	0.02	SO ₃	2.39
Total solids.....		6.160 per cent.	

The first copper-liquors contain most of the silver, and are therefore kept apart from the later liquors, poorer in this respect.

The cupric chloride is, of course, easily dissolved in the final liquor; the cuprous chloride in the presence of alkaline chlorides is

also dissolved at a higher temperature without difficulty; lastly, cupric oxide is to be converted into CuCl_2 and Cu_2Cl_2 by the FeCl_2 of the final liquor, and to become soluble thereby ($2\text{FeCl}_2 + 3\text{CuO} = \text{Fe}_2\text{O}_3 + \text{Cu}_2\text{Cl}_2 + \text{CuCl}_2$); but this could only be done by an intimate mechanical mixture of the liquor with the ore; and it is therefore preferred to dissolve merely 75 to 80 per cent. of the copper by means of the final liquor, and the remainder by further lixiviations with dilute acids. In Bräuning's paper no hint is given in what way the increase of impurities in the final liquor is prevented. No doubt only a portion of it is taken back into use, and another portion run to waste; so that there must always be a partial renewal.

Glendinning (E. P. 8602, 1885) converts the cuprous chloride in the liquors into the cupric salt by blowing in air, in the presence of at least 2 molecules of free HCl to one of salt, together with not less than 3FeCl_2 to $2\text{Cu}_2\text{Cl}_2$. [It seems certain that in consequence of this process the solution will require much more iron than before.] If arsenic be present, the excess of free HCl is to be removed by alkali or CuO ; in this case, when passing air through the liquid, most of the arsenic will be precipitated in combination with Fe_2O_3 .

Rawson (Chem. News, xlix. p. 161) describes a method for estimating cuprous chloride in copper-liquors by means of potassium permanganate.

Precipitation of the Copper from the Liquors.

This is sometimes preceded by a special treatment for obtaining the silver, which will be described afterwards. The precipitation of the copper now takes place everywhere by means of metallic iron, since the ingenious process of Gibb has been given up again. The latter consisted in precipitating the copper by sulphuretted hydrogen, which was recovered at a later stage of the process; the precipitated cupric sulphide was washed and pressed in a filter-press, and smelted in furnaces in the usual way into "coarse metal." The acid mother-liquors containing the whole of the sodium sulphate were evaporated to dryness in a furnace, mixed with small coal and reduced in another furnace; thus a mass containing nearly 85 per cent. of sodium sulphide and 2.4 per cent. of sodium carbonate was obtained. This was lixiviated with hot

water; the solution was systematically treated with impure carbonic acid, obtained by burning coke; and thus on the one hand sulphuretted hydrogen was given off, which served for precipitating the copper in the first stage of the process; on the other hand a solution of sodium carbonate was obtained, which, after evaporation and calcination, went into the trade as soda-ash. But this process was only applicable to the liquors obtained from the mechanical calcining-furnace (that is, with a minimum addition of common salt); for in the liquors from the ordinary hand-worked furnaces there would be 1 part of NaCl to each 4 parts of Na_2SO_4 , which would furnish a very weak soda-ash. This very ingenious process was worked out in all its details, and practically carried out on a very large scale, at the Bede metal-works; but it has been given up again, partly because the carbonic acid was too dear, and partly because no furnace-bottom could be constructed fit for resisting the acid liquors for any length of time—partly also because the quality of the soda-ash was too unequal—and finally because the copper was only obtained as sulphide, and had to be smelted at a greater expense than that precipitated by iron.

For this latter process either scrap wrought iron, or scrap cast metal, or “spongy iron” reduced from the residue is employed. Apart from the latter, the thinnest scrap is the best, such as the hoops of cotton or esparto bales; but as light scrap is generally rather dirtier than heavy scrap, the copper from the former is rather more impure than that from the latter. The precipitation takes place in wooden tanks exactly of the same kind as those used for lixiviation, and furnished with a steam-pipe. They are filled with scrap-iron; copper-liquor is run upon it, and steam is turned on; the heating is continued till a bright strip of iron, held in the liquid, no longer indicates the presence of copper in solution. At Oker, according to the degree of concentration of the liquors, the boiling takes place twice or three times before all the copper is thrown down; the process lasts from one to three days, and requires as much iron as the weight of copper produced, which proves that a large portion of the latter must have been in solution as Cu_2Cl_2 . Once a month the precipitated copper is removed from the tanks and washed.

After precipitation, at some works the liquor is passed through a hair sieve in order to separate the copper present in a fine state of division; the copper is washed off the residual iron by a jet of

water, or a besom, &c., and left to settle in special tanks. At other works a less rough arrangement is in use, viz. round tubs with wooden agitators, an annular place being fenced off in their upper part for the scrap iron. The agitation of the liquid causes each part of it to come into contact with the scrap iron much more quickly, so that the liquids are much sooner freed from copper than in the process first described; besides, the precipitated copper is at once washed off the iron and carried along with the exhausted liquor into settlers, and the process in the precipitating-tubs started again at once, after adding a little more iron.

A continuously acting apparatus for the precipitation of copper has been constructed by Hauch (Dingler's Journal, ccxxiii. p. 286). It consists of a cask revolving round a horizontal axis, provided with ledges inside and filled with iron borings; copper-liquor is let in, and is speedily exhausted by the rotation of the cask, the copper being at the same time washed off the iron. By combining several casks and systematically allowing the liquor to run into that cask which has been working the longest time, it is possible to obtain a continuous supply of fresh copper-liquor and a continuous running-off of exhausted liquor holding the copper in suspension. Another continuous copper-precipitating apparatus has been described by Kerpely (Wagner's Jahresb. 1877, p. 165).

The precipitation takes place most quickly by employing "*spongy iron*," as is done at the Bede metal-works. This product is made by reducing ferric oxide at so low a temperature that the iron cannot combine with carbon and cannot melt, but remains in the finely divided state, as a "sponge." This method (which may probably play an important part in the metallurgy of iron and steel, if C. W. Siemens's or Du Puy's experiments lead to a successful issue) was tried in England for the first time in 1837. Bronac and Deherrypon used it in 1859 for the precipitation of copper, but only in the dry way; but Gossage in the same year introduced the spongy iron in the wet method of copper-extraction. Further patents upon this matter were taken out by Aas in 1861 and by Bischof in 1862.

Several furnaces have been proposed for this purpose; but only one of them is in use. This is a reverberatory furnace in which the flame, after having passed directly over the charge, returns below the furnace-bed, and thus heats the charge indirectly from below. Figs. 362 to 364 show all the essential details of the furnace. It is, in the drawing, 28 feet 9 inches long; the working-bed has a

Fig. 362.

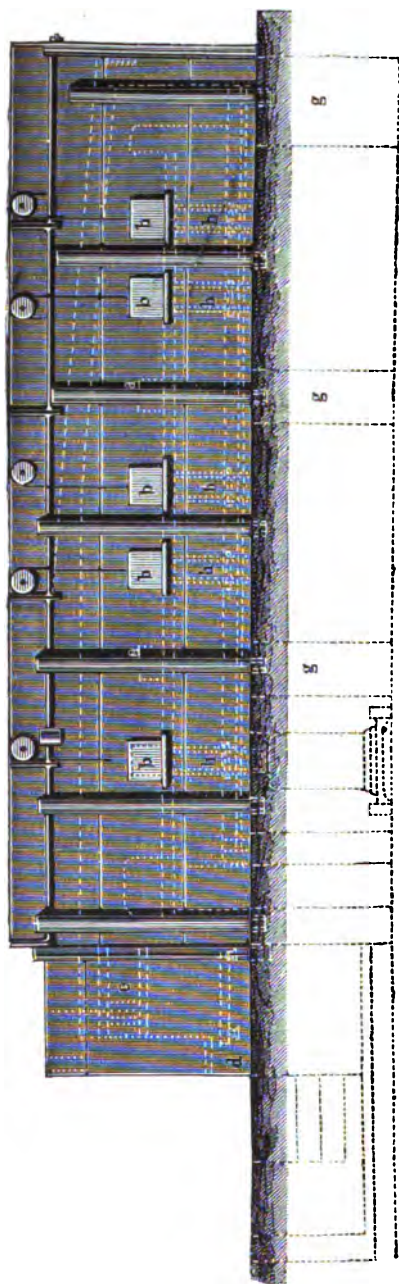
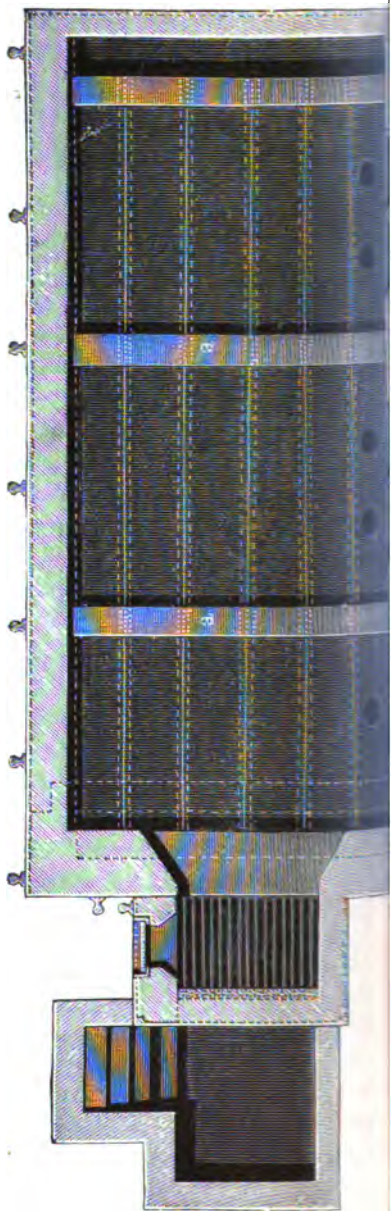
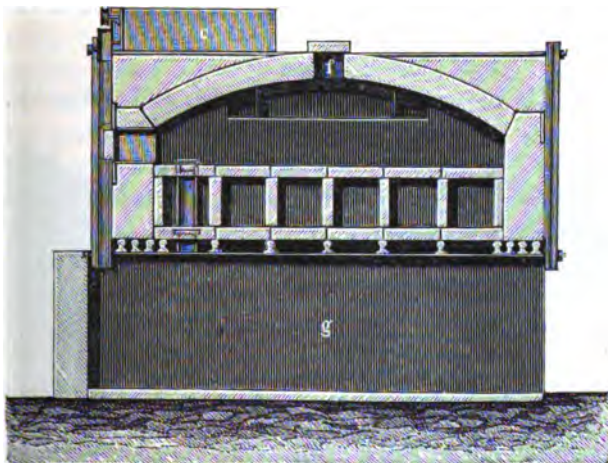


Fig. 363.



length of 22 or 23 feet and a width of 8 feet. Dwarf walls, *a a*, 9 inches high, divide it into three compartments, which on one side

Fig. 364.



have two working-doors, *b b*, each. Each compartment is charged and finished by itself. The working-doors are of cast metal, and run air-tight in frames; the same is the case with the fire-door. The fire-place is constructed for generating a reducing flame; the grate has a surface of 4×3 feet; and the bearers, *d*, are 3 feet, latterly even 4 feet 8 inches below the fire-bridge; so that a very deep layer of fuel is obtained, which does not allow any oxygen to get inside the furnace. The furnace-bed is formed by fire-tiles 4 inches thick, with rabbeted edges, partly resting upon the walls forming the divisions of the lower flues, partly upon railway-bars. The flame having travelled through these flues, descends in a vertical shaft along the fire-bridge, and thence goes to the chimney. In this descending shaft there is a fireclay damper, which is closed every time before a working-door or fire-door is opened. The 9-inch furnace-roof is surmounted by a flat cast-iron dish, *e*, supported by short pillars, for drying the ore and mixing it with coal; the mixture is charged into the furnace through the 6-inch pipes *f* carried through the arch. The whole urn ace rests on brick pillars, *g*; and the floor on the working side must be so much higher than

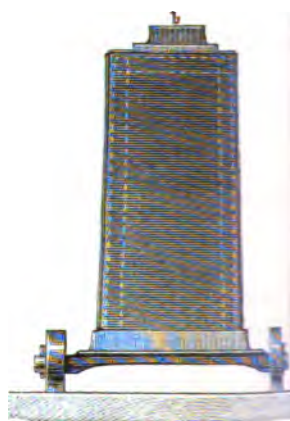
that on the discharging side, that the discharging-boxes can be run underneath the furnace between the brick pillars. The discharging takes place through 6-inch pipes, *h*, descending in front of the working-doors through the furnace-bottom and the lower flues.

The discharging-boxes (figs. 365 & 366) are made of sheet iron,

Fig. 365.



Fig. 366.



of rectangular section, tapering towards the top. The cover, *a*, is fast, and has in its centre a 6-inch opening with upright flange, *b*, by which the box is connected with the discharging-tube. The bottom of the box is movable, and turns on one side on hinges, whilst the other side is fastened by bolts and cotters. The opening in the cover is easily closed by a metal plate. The whole is mounted on four wheels in such a way that they do not interfere with the movement of the bottom. Each box has a capacity of 14 cubic feet.

When the furnace is at a bright-red heat, it can be charged. Each compartment receives a charge of 20 cwt. dry "purple ore" and 6 cwt. coals, which have passed through a sieve with eight holes to the linear inch. As mentioned, the charging takes place from the cast-iron dish above the furnace-roof. The fire- and working-doors are closed, so that the air enters solely through the

coals on the grate, care being taken that the burning mass does not become hollow, lest uncombined oxygen should get inside the furnace. The time of reduction in the compartment nearest the fire-bridge varies from 9 to 12 hours; in the second it is about 18 hours, in the third about 24 hours. The depth of the charge lying on the bed is about 6 inches. During the time of reduction each compartment must be turned over twice, or even three times. Although during this time the damper is closed, a little air always enters the furnace; but the turning-over is indispensable, as the mass would otherwise cake together. The time above stated refers to a bright red heat; a low red heat is sufficient for reduction; and the iron thus made is even better for the precipitation of copper; but as in this case much more time is required for reduction (up to 60 hours), this style of working does not pay. The fire-place being so deep, fresh coal need only be thrown in twice or three times every twelve hours, say 15 cwt. for a ton of ore.

The completion of the reduction is ascertained by testing. A small sample is taken out, put on an iron plate, covered with a brick till it has become cold, and 1 gram of the (unoxidized) central part tested by a cupric sulphate solution of known strength, which is run from a burette on to the spongy iron with frequent stirring; from time to time a drop is put on a bright blade of iron, to see whether any stain of copper is produced upon it. When the reaction in any of the three compartments is finished, the damper is closed; two of the discharging-boxes are run underneath the furnace, and their mouths connected with the discharging-pipes by an iron hoop luted with clay; then the charge is raked down into the boxes as quickly as possible. The boxes are then closed with the loose cover, run out again, and allowed to cool for forty-eight hours. They are then lifted by a crane, and the cotters are knocked out; whereupon the bottom turns upon its hinges and the whole mass of spongy iron readily falls out, owing to the box tapering upwards. The sponge is then finely ground by a heavy edge-runner 6 feet in diameter, and passed through a sieve with fifty holes per linear inch; it is now ready for the precipitation of copper.

Two different materials have been proposed for preparing spongy iron, viz. pyrites-cinders direct from the chemical works, and the 'purple ore' of the copper-works themselves. The following

analyses of average samples gives a clear idea of the chemical difference between them :—

	Pyrites-cinders. per cent.	Purple ore. per cent.
Ferric oxide	78·15	95·10
Iron	3·76
Copper	1·55	0·18
Sulphur	3·62	0·07
Cupric oxide	2·70
Zinc oxide	0·47
Lead oxide	0·84	0·96
Calcium oxide	0·28	0·20
Sodium oxide	0·13
Sulphur trioxide	5·80	0·78
Arsenic pentoxide	0·25
Siliceous residue	1·85	2·13
	<hr/>	<hr/>
	99·27	99·55

Both Bischof and Gossage proposed the direct use of burnt ore for preparing spongy iron, from the apparent advantage of utilizing its copper without the trouble of wet extraction. Unfortunately, however, the arsenic contained in the burnt ore remains in the spongy iron, gets into the copper, and greatly injures its quality. G. Bischof, indeed, in his patent of 1862, asserts that arsenic and lead volatilize; Gibb, however, admits this to be the case only for the lead to a great extent, whilst arsenic, being present mostly as arseniates of iron and copper, soon forms stable arseniurets. In fact the spongy iron made direct from pyrites-cinders contains nearly as much arsenic as was originally present in the cinders. On the other hand, the purple ore only retains faint traces of arsenic; it is therefore exclusively used for spongy iron now. The following is an analysis of the spongy iron made in the above way :—

Ferric oxide	8·15 per cent.
Ferrous oxide	2·40 "
Metallic iron	70·40 "
Copper	0·24 "
Lead	0·27 "

Carbon	7·60 per cent.
Sulphur.....	1·07 „
Alumina	0·19 „
Zinc	0·30 „
Siliceous residue	9·00 „
	<hr/>
	99·62 „

According to a more recent patent (E. P. 8093, 1884), Bischof treats iron oxide with "water gas," obtained by passing steam over incandescent coke, after having removed any steam from it by cooling. The gas is strongly heated and is passed into the lower part of an inclined retort, into the upper end of which the ore is fed, and allowed gradually to descend to the lower part. Here it comes in contact with the mixed gases, and is reduced to the metallic state by the hydrogen contained in them. The spongy iron so obtained is discharged into a receptacle and cooled before exposure to the air. The remaining gases, deprived as they are of most of their hydrogen, are still combustible, owing to the CO present; they are met in the upper part of the retort by air and are burnt, thus heating the iron-oxide preliminary to its contact with hydrogen, and making any external heating in most cases unnecessary. The operation is carried on at a low red heat.

When spongy iron is employed for the precipitation of copper, continuous stirring is required, for which at some works mechanical agitators are used, at others manual labour; at the Bede metal-works an india-rubber hose, through which a blast of air passes, is moved about in the tank. A Körting's blower would, no doubt, be the best apparatus for this purpose. Perfect mixture is thus obtained; and the precipitated copper only contains 1 per cent. metallic iron, with a great saving of space, apparatus, and labour, as against the work with scrap-iron. However, the greater cheapness of material and treatment in employing spongy iron is bought at the expense of a greater contamination of the copper by un-reduced iron oxides and carbon; at the majority of works, therefore, scrap-iron is still preferred. This, of course, depends also on the local price of the latter.

According to Bischof, with spongy iron the arsenic is only precipitated after a few hours, long after the copper has been precipitated, which thus remains free from arsenic. Gibb, however,

from many years' experience on the large scale, states that he never found any trace of arsenic in solution after the copper had been precipitated, whichever form of iron or solution of copper might be employed.

The composition of the copper precipitated by the various methods is shown by the following analyses (by Gibb) :—

	Precipitated by		
	Spongy Iron.	Heavy Scrap.	Light Scrap.
	per cent.	per cent.	per cent.
Copper	67.50	7.250	67.50
Arsenic137	.306	.100
Silver011	.046	.066
Lead	1.30	2.60	1.74
Ferric oxide	5.15	4.41	7.56
Carbon	5.10		
Silica	3.20		

At Oker the composition of the copper precipitated by scrap-iron and dried at 100° C. was :—

Cu	77.45 per cent.
Pb	0.63 "
Ag	0.10 "
Bi	0.006 "
As	0.04 "
Sb	0.15 "
Fe ₂ O ₃	6.72 "
Al ₂ O ₃	0.99 "
Zn	1.02 "
Mn	0.02 "
Co + Ni	0.03 "
CaO	0.10 "
MgO + Alkalies	2.71 "
SO ₃	4.58 "
Cl	1.19 "
Insoluble in acids	0.61 "
Oxygen + moisture (by loss)	3.654 "

100.000

Copper precipitate from pyrites-cinders made at the Witkowitz works, dried at 100° , was composed as follows (Schneider, Fischer's Jahresb. 1884, p. 162) :—

Cu	11.30	} together 69.45 Cu.
Cu ₂ O	65.31	
Ag	0.521	
Au	traces	
Bi ₂ O ₃	0.19	
Fe ₂ O ₃	3.86	
ZnO	0.45	
As ₂ O ₃	1.18	
P ₂ O ₅	0.20	
CuCl	0.32	
FeCl ₂	0.16	
CoCl ₂	0.29	
NiCl ₂	0.07	
AsCl ₃	1.32	
PbSO ₄	2.19	
Na ₂ SO ₄	3.39	
CaSO ₄	5.32	
MgSO ₄	0.59	
H ₂ O	2.98	
		<hr/>
		99.641

This product is either sent to copper-smelting works or smelted at the wet-extraction works themselves. The copper precipitated from the aqueous solutions, if kept separate from that from the acid solutions, can always be smelted directly for blister copper by adding to it lime and slags; the copper from the acid solutions is frequently so impure that it has to be mixed with raw ore, or else with soda-waste and slags, and smelted for "coarse metal," which yields blister copper only after a second roasting. Finally the usual refining takes place. At other works both precipitates are melted together, being charged at once into the furnace in the moist state. The slags produced in this operation, containing from 3 to 10 per cent. of copper, are utilized by smelting them for coarse metal (in a round blast-furnace, 3 feet wide, with four tuyeres), with the addition of soda-waste (calcium sulphide and carbonate). The mass collects in a well, where the coarse metal separates from the

slag, and the slag (a singulosilicate") continually runs off into a bogie. In order that such furnaces may be quickly taken down when the separated iron renders the smelting difficult or impossible, the upper furnace-shaft, together with its jacket, is supported on iron pillars, so that the proper smelting-shaft up to a height of 5 or 6 feet stands quite free within the pillars. The coarse metal here obtained contains about 30 per cent. of copper, and is worked up in the usual way by calcining, smelting, and roasting.

The *furnaces for smelting the copper precipitate* used at English wet-extraction works are reverberatory furnaces of the well-known Swansea type. After smelting, the slag is skimmed off, and the copper tapped as blister. When spongy iron has been used, the excess of carbon prevents the copper from being melted directly to blister; therefore about one half of the precipitate is calcined in large calciners similar to those for calcining burnt ores with salt. Here the carbon is burnt off and the copper partly oxidized; the calcined precipitate is mixed with raw precipitate and smelted, as above, for blister. The blister copper is refined by roasting to oxidize the iron, sulphur, &c., followed by reducing by charcoal the oxide of copper produced in the roasting, and poling according to the method usually employed by the copper-smelter.

The copper produced is pure and tough. It takes a good place as a marketable article; and its composition in comparison with that of English copper made by the ordinary method of smelting may be judged from the following analyses :—

	Copper from Wet Process.		"English" Copper, Field's Analyses.	
	per cent.	per cent.	B.S. per cent.	Tough. per cent.
Silver	·022	·016	·035	·047
Arsenic	·030	·170	·105	·090
Antimony	none.	trace.	·010	trace.
Bismuth	·003	·019	·035	·130
Lead	none.	·002	none.	—

The complete removal of the arsenic is said to be effected, according to a patent of Bischof's (in 1862), by precipitation with spongy iron—according to a patent of Down's (1870), by almost

completely neutralizing the copper-liquors with lime, followed by precipitation with scrap iron; the foreign metals are said to remain in solution in this case (?). Gibb declares both statements to be entirely erroneous (comp. above, p. 821); but it is quite possible that in Down's process the arsenic is removed at a previous stage, viz. on neutralizing, as ferric arseniate.

In lieu of precipitating the copper by iron, Weldon (E. P. 5607, 1882) proposed, as a cheaper process, to employ waste chloride of calcium from the Weldon process of manganese recovery or elsewhere, which produces a mixed solution of copper and sodium chloride, holding calcium sulphate in suspension. The latter is to be separated by filtration, and the copper then precipitated by lime. This process does not seem to have found practical application.

It is unnecessary to say that the copper can be precipitated from its solutions by the galvanic current, but we cannot enter into this subject in the present treatise.

Extraction of the silver contained in burnt pyrites.

According to Phillips, the cupreous pyrites-cinders contain on the average 0.0027 per cent. silver and 0.0001 per cent. gold. These metals on calcining with salt are converted into chlorides; and, owing to the solubility of AgCl in NaCl , the silver is found mostly, the gold at least partly, in the liquors obtained by lixiviating the calcined ore. In order to further this, Phillips adds some more common salt in the lixiviating tanks. These metals are now recovered in most works, usually by the process of Claudet (1871). This process consists in precipitating by a soluble iodide the silver from the liquors in the state of AgI , which is quite insoluble in solutions of chlorides. Only the first three liquors (which contain 95 per cent. of all the silver) are employed; the diluted state of the other liquors would make the recovery of the silver from them unprofitable. The liquors, before they undergo precipitation with iron, are completely settled, run into a gauged tank, and their contents of silver accurately estimated by adding to a certain volume muriatic acid and a solution of lead acetate, and afterwards potassium iodide. The precipitate is collected on a filter, washed, dried, and fused with a flux of soda, borax, and the finest carbon. The lead regulus obtained is cupellated; and from the weight of the silver

thus obtained, that contained in the liquors is computed. To the liquor a solution of potassium or zinc iodide of known strength is now added in sufficient quantity to precipitate all the silver; the iodide solution is diluted to such an extent that it amounts to about $\frac{1}{10}$ the volume of the liquid; the precipitate is allowed to settle; the clear liquor is tested in the laboratory to see if all the silver is thrown down; and if so, it is run into the tanks for precipitating the copper, where it is treated in the usual way. The quantity of iodide employed for the precipitation is much larger than that corresponding to the silver present, since a portion of the lead is thrown down as PbI_2 . Probably the silver is precipitated before the lead; but as it is not possible to bring all the silver contained in the liquor into contact with the iodide before the latter has also come into contact with molecules of lead, the precipitate always contains a good deal of lead; so that necessarily a corresponding excess of the precipitant is required.

The precipitate, consisting mainly of AgI , PbI_2 , and PbSO_4 (which falls down on the liquor cooling), is well washed with water; and if a sufficient quantity of it has been collected, it is treated in the moist state and hot with metallic zinc and a little muriatic acid. Thus the AgI and PbI_2 are decomposed completely, the PbSO_4 partly, and a liquor containing *zinc iodide* is obtained, which is employed over again for precipitating argentiferous liquors in proportion to its percentage of iodine. On the other hand, a metallic sponge, mixed with pieces of zinc, is obtained having the following composition:—

Ag	5·95
Au	0·06
Pb	62·28
Cu	0·60
ZnO	15·46
Fe_2O_3	1·50
CaO	1·10
SO_3	7·68
Insoluble residue	1·75
Oxygen and loss	3·62
	<hr/>
	100·00

This is sent to the silver-works. Usually the argentiferous copper-

liquor is first mixed with the solution of ZnI_2 , obtained in reducing the AgI &c., and the last portion of the silver precipitated by KI . A certain loss of the latter is unavoidable, whatever care be taken. In this way Phillips obtains about two thirds of the total silver contained in the burnt ore, and about a similar proportion of the gold; several others have not been content with this, and have given up the process, probably because sometimes on calcining with salt too much Cu_2Cl_2 is formed (its quantity varies from 0 upon 6.70 CuCl_2 , to 0.62 Cu_2Cl_2 , upon 3.75 CuCl_2), and in its presence the silver seems to be incompletely precipitated by iodides. At Phillips's works special care is taken to avoid the formation of cuprous chloride; and, perhaps on this account, Claudet's process has been more successful there than elsewhere.

An improvement on Claudet's process is asserted to be offered by the process of E. L. Mayer, patented in 1877. The copper-liquor is precipitated with a solution of glue and KI ; the solution contains very much copper and only a few thousandths per cent. of Ag . After the precipitate has settled down, a solution of tannin is added and a little more precipitate obtained. The precipitates are washed with similar dilute acid as serves for dissolving the copper-ores in order to remove the copper they may contain. The acid is neutralized with lime, and treated with alkaline sulphides in a revolving drum till all iodine is removed; the solution containing iodides can be used for again precipitating silver. The remaining sulphides of lead, silver, &c. are to be worked for silver. The addition of glue and afterwards of tannin has for its object to conglomerate the extremely finely divided AgI (of which otherwise a portion would escape collection) into a larger mass.

Another process was proposed in 1873 by W. Gibb. It is based on the observation, that if a copper solution containing very little silver is treated with sulphuretted hydrogen, by far the largest portion of the silver is thrown down as Ag_2S with the first portions of CuS . The H_2S is made from the tank-waste of alkali-works by treatment with dilute hydrochloric acid in wooden vessels; the hydrochloric acid enters the vessel underneath a false bottom made of boards covered with furnace-slugs, and runs out near the top completely saturated. The vessels need not be air-tight, as the gas is aspirated from them by an air-pump, the delivery-pipe of which is provided with branches for every one of the precipitating-

tanks; an india-rubber hose conveys the gas into these, and, when moved about in the liquid, sufficiently agitates it by the escaping gas. The process is continued until as nearly as possible 6 per cent. of the copper has been precipitated, which generally takes 20 minutes. The bulk of the copper, which otherwise shows on the average 18 ounces of silver per ton, shows after this treatment only 2 to 4 ounces. The 6-per-cent. CuS precipitated at first, however, contains 200 ounces silver per ton. The dilution of the gas by air seems to be favourable to the process. The precipitate is allowed to separate into clear liquor and denser mud; it is washed several times by decantation, and then pressed in a Needham's filter-press. The damp sulphides are calcined in an ordinary calciner; the product contains one fourth of the copper as sulphate, the remainder as oxide or oxychloride, and the silver altogether as chloride. It is roughly ground, washed with water, and the solution of CuSO_4 , which only contains 1 ounce of silver to the ton of copper, precipitated as usual. The residue, mostly CuO , is systematically extracted by hot concentrated solution of common salt, which dissolves nearly all the silver, leaving only 3 to 4 ounces of silver per ton of copper in the residue. The solution containing the silver is precipitated by milk of lime, the precipitate washed with water to remove the CaCl_2 , then with dilute sulphuric acid to dissolve the copper, then again with water, and leaves at last a residue containing 9 per cent. of silver as AgCl , worth £700 per ton. It contains besides principally the sulphates of calcium and lead. This treatment is said to cost 9*d.* per ton of burnt ore, and to yield about $\frac{1}{2}$ ounce of silver, of the value of 2*s.* 6*d.*; but, in this shape, it appears to have been given up again.

Chadwick and Jardine, in 1875, patented a new desilverizing process, which is said to be in use at Henderson's works at Irvine. The copper-liquors are diluted to 20° or 25° Tw., and a very weak solution of lead acetate added, which is equivalent to the whole of the Ag, As, Sb, and Bi, less any Pb already contained in the pyrites. Usually about 230 grams of brown sugar of lead per ton is used. On agitating, a light-yellow precipitate is obtained, consisting of 53 per cent. lead sulphate, 5–6 per cent. silver sulphate, and 3 ounces of gold per ton of precipitate (say, 0·01 per cent.). After thorough washing, the gold and silver can be obtained by smelting and refining in the usual way. The copper is said to be thus obtained free from As, Sb, and Bi.

According to a patent of Snelus (1875), finely divided iron dust is to be injected by a blower into the copper-liquors, just sufficient to precipitate 19 per cent. of all the copper; this is said to carry down 80 per cent. of all the silver contained in the solution.

A new patent by Phillips (No. 3923, Oct. 10, 1877) prescribes mixing the copper precipitate with common salt and soda, moistening with water, and grinding in a pug-mill to a paste. The mass is dried and calcined in a reverberatory furnace, constantly stirring, till all the copper has been converted into CuO and all the silver into AgCl . The alkali added decomposes any volatile copper salt present, and almost entirely prevents any volatilization of silver during the calcining process. The AgCl is extracted from the calcined mass by treatment with a hot solution of common salt. (This is essentially like Augustin's process of 1840, applied to the extraction of silver from ordinary ores.)

Thilo (Chem. Zeit. 1886, p. 822; J. Soc. Chem. Ind. 1886, p. 548) gives special prescriptions for estimating the very small quantity of silver (0.003 to 0.008 per cent.) contained in pyrites-cinders.

Waste Liquors from the copper extraction.

Utilization of the sodium sulphate contained in the mother-liquors from the precipitation of copper.—We have mentioned above the process of Gibb and Gelstharpe (p. 813), which has been given up again. At present the acid mother-liquors are everywhere let run into the rivers, and the sodium sulphate contained in them is lost. At a large copper-works for a time a process was employed by which ferric oxide was simultaneously obtained of great purity and fineness, so that it could be sold on the large scale for red paint. The acid liquors were boiled down to dryness in a brick furnace; the residual mass of sodium sulphate and chloride and iron salts was ignited, and ground very fine under edge-rollers; it was then carefully calcined in an ordinary calciner until all the iron salts were peroxidized. The mass was treated with hot water and allowed to settle; the ferric oxide deposited only required washing in order to become marketable as Venetian red. The solution (containing chiefly Na_2SO_4 and NaCl) was concentrated in pans by means of steam circulating in a worm, an agitator preventing the salt from adhering in crusts to the bottom and sides of the pan and to the

worm. At a concentration of 1.37 to 1.40 sp. grav. nearly all the sulphate was found to be separated; the liquor with the suspended salt was drained off the precipitate, which was washed with a little hot water and dried in a furnace. It contained only about $\frac{1}{2}$ per cent. of NaCl, and not a trace of iron; so that it was very well adapted for glass-making. The high price of coals caused this process to be given up at the time; and it does not seem to have been taken up again. Probably the first step, viz. the evaporation of the acid liquors in a brick furnace, would present the same difficulties as in Gibb's process.

Ellis (J. Soc. Chem. Ind. 1884, p. 613) proposes, in lieu of concentrating the liquors by heat, to do so only partially, and then to promote the crystallization of sodium sulphate by cooling. He mentions no trials made on the large scale.

E. de Cuyper (G. P. 53,261 and 54,131) cools the liquor down to -3° , at which temperature all the sulphate of soda crystallizes out, whilst the chlorides of iron, zinc, sodium, &c. remain in solution even at -10° C. After removing the Glauber's salts, the liquor is boiled down to dryness and the residue is calcined; pure ferric oxide is formed and is freed from the zinc chloride by lixiviation.

Jurisch (G. P. 41,737) seeks to utilize the waste liquors after extracting the copper in the following manner. They are almost neutralized, in tubs provided with mechanical agitators, by means of calcium carbonate; air and steam are blown through, and in the same ratio as ferric sulphate is formed milk of lime is added, without, however, allowing all the acid to be saturated. When all the iron has been precipitated the mud is run into the settlers, the clear liquor is drawn off, and the deposit is passed through a filter-press. It contains some zinc salt, calcium sulphate, and carbonate, and can be made richer in iron by employing it the next time for the saturation of fresh liquor. The basic sulphate of iron thus formed can be employed for making sulphuric anhydride, oxide of iron, paint, &c. The liquor drawn off from it is mixed in an agitator with enough milk of lime to produce basic reaction; the zinc hydroxide precipitated contains some basic ferric sulphate, manganese, and calcium carbonate, and can be utilized in suitable manner.

According to a communication of the inventor in the 'Chem. Ind.' 1888, p. 3, 50 cubic metres of waste liquor, containing 40 grams ZnCl_2 per litre (from pyrites containing 1.5 to 3 per

cent. Zn), would yield by his process 806 kil. ferric oxide mixed with calcium carbonate, 3600 kil. ammonium sulphate, 1444 kil. zinc oxide (50 per cent. Zn), 3245 kil. common salt, and a little potassium chloride. This is, however, only derived from analyses and laboratory trials, as Jurisch's process has not found any practical application. It will be interesting, though, to quote from his paper the composition of the liquor he worked with, obtained from the Witkowitz iron- and copper-works, with Hungarian pyrites.

1 litre contained :—

8.6	grams	free	HCl,
73 0	„	„	Na ₂ SO ₄ ,
3.6	„	„	K ₂ SO ₄ ,
16.9	„	„	NaCl,
40.3	„	„	ZnCl ₂ ,
25.9	„	„	FeCl ₃ ,
3.1	„	„	FeCl ₃ ,
6.4	„		other matters.

He also gives a table of the copper and zinc percentages of a great many descriptions of pyrites.

Wigg, Steele, and Wigg (E. P. 13,722, 1884) mix the waste liquor with waste chloride-of-calcium liquor from the Weldon process in equivalent proportions, when a white bulky precipitate of calcium sulphate is formed, which is filter-pressed and sold as "pearl-hardening." The filtrate is treated with milk of lime, which precipitates ferrous hydrate, and this is oxidized by injection of air or chlorine, washed in a filter-press, and furnaceed to yield paint of various shades. Another patent of Wigg's (5620, of 1885) prescribes precipitating the iron by means of ammonium sulphide, and a third patent (11,129, 1885) describes apparatus for these treatments.

Bird's patent (12,458, 1887) seems to contain no essential new feature.

Other copper-extracting processes.

P. Spence (comp. Inspectors' Report, 1877-78, p. 48) burns the pyrites (finely ground) in a furnace provided with mechanical stirrers that plough up the ore into ridges, making a change of surface every $2\frac{1}{2}$ minutes (comp. p. 264). He asserts that in this way he burns three tons of ore in a furnace in a day, and renders all the copper soluble to 0.24 per cent.; thus he is able to wash

out the copper-salt and avoid the subsequent roasting with common salt. As much as 4·6 per cent. of sulphuric acid is left in the ore, rendering the copper soluble.

H. and Ch. H. Hills (E. P. 1621, 1878) separate the coarse and fine portions of pyrites-cinders by sifting. The fine portions are calcined with salt in the usual manner; the coarse portions are lixiviated with dilute hydrochloric or sulphuric acid, and the copper is precipitated from the liquor by means of iron.

A very similar process of extracting copper from pyrites-cinders has been described by Jetzler ('Dingler's Journal,' ccxvii. p. 478). He worked pyrites from Borsa-Bánya, in Hungary, containing only 1·01 Cu. The burnt ore decays easily on lying in the air; and after sifting off the not decayed core through a sieve with 10 meshes to 1 centim. square, the copper can be extracted by hot weak muriatic acid of 3°–4° Tw.; probably Fe_2Cl_6 acts here, chlorinating the lower sulphides of copper, and being reduced to FeCl_2 . On washing, solutions of 24° Tw. are obtained, which, besides copper, contain Ag, Pb, $\text{Al}_2(\text{SO}_4)_3$, &c. The metals were precipitated by scrap iron; and the precipitate was sold to a smelting-works according to its value of Cu and Ag. The process did not pay very well, as the residue could not be used as an iron-ore.

Another process has been patented (in 1873) to Baron Leithner in Austria ('Dingler's Journal,' ccxi. p. 349). The burnt ore (in this case containing about 1 per cent. of copper) is to be smelted with 36 per cent. calcium hydrate in a kiln heated by the waste gas of a blast-furnace; the product is to be smelted for pig-iron, which now contains 2·09 per cent. Cu; and this is to be used for precipitating copper; so that its own copper is utilized as well.

Some patents of Mason's (Nos. 2984, 2992, and 2993, 1877) seem to contain nothing of any importance that is new.

The whole of the processes connected with the wet extraction of copper, as far as published up to the end of 1878, and including many proposals or actually employed processes not mentioned here (because they do not refer specially to the treatment of pyrites-cinders from sulphuric-acid works), are described in a condensed form by Bode (Dingler's Journal, ccxxxi. pp. 254, 357, 428).

The patents of Hargreaves and Robinson (E. P. 5601, 1886, and 3704, 1887) for extracting gold, silver, and copper from pyrites can be only mentioned in this place.

General.

According to Hunt's 'Mineral Statistics' for 1874, p. 65, there existed in Great Britain in that year 22 copper-works for wet-extraction, which together consumed 329,000 tons of burnt ores (say, equal to 450,000 tons of pyrites). Two of them made blue copperas; three went as far as refined copper; the others sold their precipitate to copper-smelting works. The total production of copper from this source in 1874 amounted to 9000 tons. In 1882 the quantity of burnt ore worked for copper was 434,427 tons, containing 15,300 tons of copper.

On laying out a copper-extraction works the levels must be carefully attended to, so that the very large quantities of solid substances and liquors may be easily moved about. At Oker, Hebburn, &c. all the apparatus are arranged at different levels. The design of the Oker works has been published by Bräuning (comp. p. 786). The top level is occupied by the charging-loft, to which the burnt ore and the salt are brought by bogies; attached to it are two edge-runners, each of which grinds daily 15 tons of ore and $2\frac{1}{2}$ tons of salt down to a size of 2 millims. The mixture is taken by bogies to the furnaces, situated at a little lower level; the furnaces are heated by gas-producers, situated still lower down. Below the furnaces there follow, at three descending levels, the lixiviating-tanks, the precipitation-tanks, and cisterns for the "final liquor," from which it is pumped up again by injectors and used for lixiviating fresh ores.

CHAPTER XV.

THE MANUFACTURE OF NORDHAUSEN OR FUMING OIL OF
VITRIOL, AND OF SULPHURIC ANHYDRIDE.

In the third Chapter the fuming or "Nordhausen" oil of vitriol has been described, and has been characterized as a mixture of

sulphuric hydrate and pyrosulphuric acid, $\begin{array}{c} \text{SO}_2\text{—OH} \\ \text{>O} \\ \text{SO}_2\text{—OH} \end{array}$, a compound

which latterly has come into the market as "solid oil of vitriol."

Although in all probability the fuming oil of vitriol is precisely that kind of sulphuric acid which was obtained first of all, and although a generation ago it was manufactured in several places, and especially near Nordhausen, in Prussian Saxony, latterly its manufacture according to the only method formerly employed has been carried on exclusively in Bohemia, by the firm of Johann David Starck. The reason of this was that in this manufacture manual labour constitutes a very large portion of the expense, and that it requires a very large space and a great number of small apparatus, so that it can only pay under certain conditions rarely present. Owing to this, all other factories have ceased to work, even those in the Harz (which, by the way, were not located at Nordhausen itself, where there was only a warehouse for the acid, but at Braunlage and Goslar).

So long as fuming oil of vitriol was only used for dissolving indigo (for which purpose it is very little employed now), the monopoly of the Bohemian firm was not very much felt; but since very large quantities of fuming acid were required for refining ozokerite and especially in the manufacture of alizarine and many other coal-tar colours, many efforts have been made at producing that acid in

another way; and success has at last been attained. The attempt has been made in two ways:—first, by trying whether the ferric sulphate obtained by the Bohemian method cannot be replaced by other sulphates yielding their acid on heating, partly or entirely as anhydride; and, secondly, trying whether the anhydride (as a solution of which in sulphuric hydrate the “oleum” can be viewed) cannot be obtained synthetically.

These methods shall be mentioned later on; we must, however, in the first place describe the method by which the oil of vitriol was formerly exclusively supplied—namely, from “vitriol stone”—which rests on the fact that ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, at a red heat splits up into ferric oxide (Fe_2O_3) and sulphuric anhydride (3SO_3), the latter of which is partly decomposed into SO_2 and O.

The manufacture of fuming oil of vitriol in Bohemia.

All former descriptions of this manufacture have been made obsolete by that given by E. V. Jahn in Wagner's ‘Jahresbericht,’ 1873, p. 220. We shall give an abstract of the latter, adding some supplementary notes.

The basis of the whole manufacture is constituted by the Przibram slates, belonging to the Silurian formation and lying directly over the palæozoic clay-slate. They are of different kinds: either they are quite similar to the palæozoic clay-slates and can be partly used as roofing-slates (these are called “dead slates”), or they contain coal and from 1 to 31 per cent. of pyrites. The latter can be readily distinguished by their darker colour and considerable specific gravity; they are called “alum-slates,” or, more appropriately, “copperas-slates.” They occur in large seams, up to 20 fathoms thick, at the edge of the Pilsen-Wald beds; they are most frequently met with at the banks of watercourses, where the water has denuded the surface, and are distinguished by their oxidability and frequent efflorescence of copperas. Sometimes their influence, where they have been confounded with the less-decaying slates in erecting railway embankments &c., is felt in a very unpleasant way. The oxidability of the copperas-slates has led to a special industry, which has existed since the 16th century. When rich in alumina (which is only exceptional), the slates serve for making alum; when poor in alumina and rich in pyrites, for copperas and “vitriol stone”

(*Vitriolstein*), i. e. ferric sulphate—from which naturally followed the manufacture of fuming oil of vitriol. The Pilsen sulphur-works are already mentioned in 1526; the fuming oil of vitriol is the oldest form of sulphuric acid, and was first manufactured in Bohemia, whence it was driven by the horrors of the thirty years' war and the following horrors of the counter-reformation; and the Nordhausen country received it. For some time past, however, that industry, having ceased to exist near Nordhausen, has returned to its old home in Bohemia, where it was favoured by the presence of large stores of fossil fuel in the immediate vicinity of the copperas-slates. Since 1778, at Gross-Lukavic, the manufacture of oleum has been resumed, but only since 1792 on a larger scale, when Johann David Starck took it in hand, at first with the assistance of men obtained from the Nordhausen factories. He first used calcined copperas, then "vitriol stone" bought at Altsattel. He also made larger quantities of ordinary sulphuric acid, and advanced the whole industrial development of that country to such an extent that in 1836 he was ennobled. The firm is still carried on by his son, who has all but monopolized the manufacture of fuming acid, which, however, is only one of the branches of his enormous establishments, yearly putting into the market goods to the value of nearly half a million sterling. The principal seats of the manufacture of fuming vitriol are at Bras, Kasnau, Bykov, and Davidsthal. It consists of three branches:—1st, the production of the vitriol stone; 2nd, the distillation of "oleum;" 3rd, the production of "caput mortuum."

The production of vitriol stone originally took place from the mother-liquors of copperas- and alum-making, which principally contain ferric sulphate; but it now comes chiefly from the copperas-slate ("Vitriolschiefer"), of which Anthon has given the following analyses:—

	From Weissgrün.		Darova.	Hromic.	Briza.
	I.	II.			
Soluble in water:—					
Sulphates of Ca, Mg, Fe	1.20	2.80	1.00	1.60	0.50
Insoluble:—					
Iron sulphide	12.37	31.53	14.50	11.58	14.33
Ferric oxide	0.76	2.17	2.42	0.16	0.61
Alumina	3.50	2.40	2.80	1.20	1.30
Silica	74.90	55.96	71.21	75.70	73.40
Carbon	6.09	4.99	6.84	8.40	8.80
CaO, Cu, Se, As, loss	1.18	0.15	1.23	1.36	0.73
Specific gravity.....	2.76	3.15	2.67	2.56	2.85

The value of the slates does not depend upon their appearance, least of all upon that of visibly crystallized iron-pyrites, which is not easily oxidized, but upon that of iron sulphide in an extremely fine state of division, which exists especially in the last two varieties. These decompose so completely that after a few years nothing but loose carboniferous silica is left behind. From this it follows that the calcining of the copperas-slates (formerly employed) not only did no good, but much harm, by driving off a good deal of sulphur as SO_2 . The largest plant for producing the copperas-slate is at Hromic, where a seam of 20 fathoms thickness exists at a depth of 11 fathoms. Between the years 1831 and 1871 650,000 tons of suitable ore were got here; and altogether about $9\frac{1}{2}$ millions of tons are available. At Littau there are about 7 millions of tons; and so forth. The ore is broken up pretty equally by stone-breaking machines, and tipped into large terrace-shaped heaps, leaving both horizontal and perpendicular air-channels. By means of a system of spouts water can be sprinkled all over. The process of oxidation by weathering lasts about three years; and very large heaps having been made at first, strong lyes are always obtained. The ores, on lying in the moist air, grow hot; the pyrites is oxidized, first to ferrous sulphate, then to ferric sulphate, along with a little aluminium sulphate. These salts, together with the pre-existing soluble salts, are lixiviated by water conveyed in the above-mentioned spouts. The brown liquors, possessing a density of generally 28° , and up to 38° Tw., are run into wooden reservoirs, where they remain some time for settling and are a little concentrated by spontaneous evaporation and also more highly oxidized. Then they are concentrated, by top-heat in brick-furnaces, up to 77° Tw.; the soot and ashes are allowed to deposit in settling-tanks; and the clear liquor is further evaporated in cast-iron boilers to a sirupy consistence. If then run on to the floor, it solidifies to *crude vitriol stone*. This is a hard, pale green or yellowish-green mass, containing still a good deal of ferrous sulphate and water of crystallization. In order to remove the latter and to oxidize the former, it is calcined in open roasters. The *calcined vitriol stone* is essentially anhydrous ferric sulphate; it is yellowish white, dissolves in water with a reddish-yellow colour without leaving any large residue; and the solution has a strongly acid reaction. It still contains a little ferrous sulphate and constantly, in variable quantities, aluminium sulphate along with a little magnesium and

calcium sulphates. The production of vitriol stone at Hromic, Littau, and Weissgrün in 1872 amounted to about 3000 tons; it takes from 6 to 20 tons of slates to make one ton of vitriol stone. The stone formerly only yielded about 33 per cent. of "oleum;" now, however, owing to improved processes, it yields from 40 to 50 per cent.

The firm of J. D. Starck works up the stone in 4 works, altogether with 120 "oleum-furnaces." These are the galley furnaces, well known from older technological works. The calcined vitriol stone is broken by crushing-rollers and charged into the oleum-retorts, made of fireclay. On each side of the galley furnace there are four tiers of 34 retorts each, the bottoms of those in the centre nearly touching one another. A fifth tier is formed at the top by 34 large retorts, open at either side, reaching right across the furnace, and at each side provided with a receiver. Each of the smaller retorts also is connected with a receiver, large enough for holding the product of 4 or 5 distillations. The necks of the receivers are narrower than those of the retorts; they are put into the latter, and the joint plastered with clay. Such a furnace thus contains 272 small and 34 large oleum-retorts and 340 receivers. The lower part of the furnace, where the fireplace, grate, and ash-pit are located, is made of solid masonry; the upper part consists of a light arch, perforated for each retort in such a way that the necks of these hold them without any further support. The bottom tier of the receivers rests upon the brickwork, the higher tiers on wooden laths.

Into each retort is ladled, on the average, 750 grms. of vitriol stone. The yearly consumption at Starck's works is 724,000 retorts and 40,000 receivers (formerly twice as much). They are made at private potteries near the works, and thus only cost about 1*d.* to 1½*d.* a piece, whilst formerly, when bought abroad, they cost about 3*d.* each.

At the beginning of the distillation the temperature is slowly raised, so that after 4 hours the bottom tier of retorts has only attained a red heat. During this time the retorts are left open; and consequently nearly all the ferrous sulphate still present is oxidized to ferric sulphate. With a higher heat there appear at the mouth of the retorts aqueous vapour and sulphurous acid, generated from aluminium sulphate and still existing ferrous sulphate. Now thick vapours of sulphuric anhydride follow, which gives the sign for putting on the receivers. As the ferric sulphate

simply splits up into Fe_2O_3 and SO_3 , but the "oleum" is a variable mixture of SO_3 and SO_4H_2 , or rather of pyrosulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$) with sulphuric acid, some liquid containing water must be put into the receivers, in order to condense and dissolve the sulphuric anhydride. This may be either rain-water or ordinary (so-called "English") oil of vitriol. In the former case each receiver gets $\frac{1}{2}$ lb. of water, and it takes 4 or 5 distillations from the retort to attain the usual concentration of the oleum (79° Baumé). When the receivers have been charged with "English" oil of vitriol, of 66° Baumé ($= 168^\circ$ Tw.), it only takes 3 or 4 distillations to get it up to 80° Baumé.

When the oleum has reached sufficient concentration, which the workmen recognize from the speed with which a wood splinter, dipped into it, is charred, it is filled into stoneware bottles and left for a week to settle, after which time the clear acid is drawn off from the deposited mechanical impurities. The specific gravity is sometimes artificially increased by addition of anhydrous sodium sulphate, to which practice, as Mr. E. V. Jahn in his report naïvely remarks, the consumers decidedly object. When "English" oil of vitriol has been put into the receivers, the oleum of course contains the well-known usual impurities of the former.

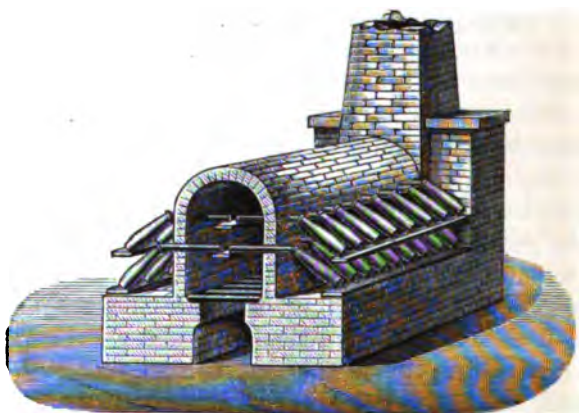
The ferric oxide remaining in the retorts (about $33\frac{1}{2}$ per cent.) is known by the name of caput mortuum, colcothar, English red, &c. (In England a similar article is called "Venetian red.") It is raked out of the retorts after each distillation, and exhibits different colours according to the degree of heat to which it has been exposed. The lower tiers supply it of darker, the upper ones of lighter colour. In the crude state it was very difficult to sell as a common pigment or polishing-powder; in 1832 about 250 tons of it were sold. J. D. Starck has very much improved this article by proper treatment; so that in 1872 1000 tons of it were sold, of 19 shades and 41 grades; it is especially used at Hamburg for painting ships. At the Bras works it is ground under French mill-stones and again calcined with the addition of common salt and at a certain temperature. The yellow shades are obtained by an addition of 2 per cent. of salt, igniting for an hour, and gradual cooling in a closed space; the brown ones, by adding 4 per cent. of salt; the purple ones, by 6 per cent. of salt, igniting for 6 hours at a gradually increasing heat, and rapid cooling. The igniting takes place in fireclay pipes lying in galley furnaces similar to the oleum-furnaces, each of them containing 60 pipes. Unless the temperature is exactly regulated, the

product becomes dark brown, and is then of little value. The best is contained in the two top tiers. After the igniting and cooling, it is sifted and levigated; by mixing the three above-named principal shades the commercial shades between yellow, purplish red, and dark purple are obtained, which now only require drying and packing.

The smallness of the retorts used for decomposing the vitriol stone, and the large number of these apparatus consequently necessary, are evidently to be explained by the fact that in larger apparatus the heat would penetrate too unequally and would cause great loss by overheating one part and insufficiently heating another part of the charge.

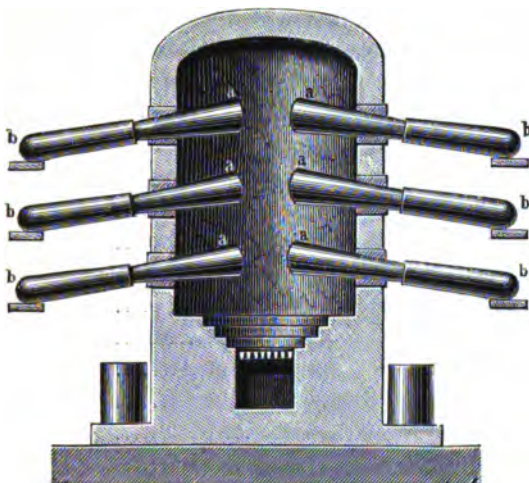
The following drawings of galley furnaces so far deviate from the preceding description, that in the place of five tiers of retorts only two or three are shown. Fig. 367 (from Knapp) represents a two-

Fig. 367.



tier furnace in perspective view, fig. 368 (from Kerl-Stohmann) a three-tier furnace in section. In both cases, erroneously, the neck of the retort is drawn as entering that of the receiver; whilst the opposite is the case, so that the luting cannot get into the receiver. The retorts are pear-shaped, 10 in. long, at the bottom $2\frac{1}{2}$ in., in the middle $4\frac{1}{2}$ in., at the mouth $3\frac{1}{4}$ in. wide, with walls half an inch thick. The receivers have nearly the same shape; but they are longer, and narrower in the neck. The luting consists of clay and sawdust. Each distillation takes 36 hours; the end is known by the receivers getting cold. The fire is then allowed to go out, the

Fig. 368.



furnace allowed to cool for 12 hours, the hardened luting broken by a few taps with an iron tool, and the receivers taken off. The contents of the latter are not emptied into the well-known stoneware bottles, closed by screw-plugs, until they have become sufficiently concentrated—that is, after 4 or 5 operations (see above); the retorts, however, are cleared out every time, by raking out the caput mortuum, and are tested by tapping to see whether they are still sound. If not, they are replaced and the distillation at once begun with a fresh charge. Formerly each distillation in a furnace of 288 retorts required 30 new retorts and 3 new receivers; now there is less breakage. The fuel is wood well dried, or lignite.

Payen gives the following cost-account of 100 kilog. oleum (now, of course, obsolete):—

	frs.	ct.
250 kil. vitriol stone	14	0
2000 kil. lignite	3	0
Wages	8	0
4 retorts and 4 receivers (?)	2	0
Interest.....	1	80
	<hr/>	
	28	80
125 kil. residue, value.....	2	0
	<hr/>	
Cost of 100 kil. oleum	26	80

The communication of Stolba (Fischer's Jahresb. 1885, p. 316) adds nothing essential to that which was previously known. We will only quote the statement that in 1884 the quantity of oleum produced in the Pilsen district amounted to 4349 tons, made by 38 workmen, and the following analyses:—

1. *Vitriol Stone.*

Ferric sulphate	50·17
Aluminium sulphate	11·94
Ferrous „	1·35
Magnesium „	1·17
Calcium „	0·33
Copper „	0·20
Sodium „	0·11
Potassium „	0·13
Sulphuric acid	1·49
Silicic acid	9·10
Traces of Mn, As, P ₂ O ₅	—
Water	23·31
	<hr/>
	99·30

2. *Caput mortuum.*

Ferric oxide	74·62
Alumina	12·53
Magnesia	3·23
Lime	0·82
Sulphur trioxide	5·17
Silicic acid	1·17
Copper oxide	0·20
Water	1·30
	<hr/>
	99·04

From a private source we can add that under the most favourable circumstances the yield from 100 parts of ferric sulphate, with 52 to 54 per cent. SO₃, is hardly 36 parts of sulphuric anhydride testing 95 to 96 per cent., which is, of course, dissolved in the acid contained in the receivers.

An important improvement in the manufacture of Nordhausen acid by the Bohemian process, which is also applicable to the manufacture of SO₃ from ordinary sulphuric acid, has been pro-

posed by R. Schuberth (G. P. 52,000). He states that the formation of sulphurous anhydride is the principal cause of the loss which, in the best case, amounts to 30 per cent. of the total SO_3 , and in the case of large vessels or furnaces may destroy all the SO_3 present. This is caused by the prolonged contact of free SO_3 with the red-hot sides of the retorts, and this circumstance has hitherto confined the Bohemian process to the use of small vessels, involving a large consumption of fuel and of clay retorts, together with the necessity of employing much skilled labour and other drawbacks, such as the escape of acid smoke into the atmosphere. All this is avoided by bringing about the decomposition of the sulphates in a partial vacuum, and removing the vapours away by aspiration. This can be done with ferric sulphate obtained in the Bohemian manner from schist, or with artificially prepared sulphates of iron &c. The operation is carried on in a horizontal shallow fireclay retort, provided with a cast-iron mouth-piece like that of gas-retorts. This mouth-piece contains an opening for charging and discharging, and a stirring-rake sliding in a stuffing-box; when not at work, the rake is pulled back towards the front so as to be out of the heated portion of the retort. Above the furnace there is placed a cast-iron tube, containing a suitable filtering-substance for the gases, such as broken glass or pottery, arbestos, glass-wool, and the like. This gas-filter communicates on the one side with the retort, on the other side with a cast-iron air-pump. The vapours, drawn by this pump from the retort and passed through the filter, are forced through an upright cast-iron cylinder, lined with earthenware and containing a number of perforated dishes, charged with 10 per cent. platinized asbestos. The apparatus is heated by the waste gases from the retort-fire and serves for regenerating SO_3 from the small quantities of SO_3 and O formed in the retort. From here the vapours pass into cast-iron condensers, where they are absorbed by strong sulphuric acid, the condensation being aided by pressure. During the operation the sulphate within the retort is raked up several times; but while this is done, the pump is stopped in order to avoid any dust being drawn away. The employment of a vacuum causes a quick decomposition of the ferric sulphate, with but slight formation of SO_3 ; the duty performed by the apparatus is large, and the consumption of fuel much less than before. The residue is not overheated, as is the case in the lower ranges of the galley furnace,

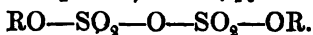
and is thus better adapted for use as a paint; from the same reason it is also possible to use it over again for forming ferric sulphate. If sodium sulphate is to be used, the retort is made with a dished bottom, lined with platinum. This is charged with sodium sulphate once for all; by adding sulphuric acid of 140° Tw. bisulphate is formed, which (in the same way as is done in the case of ferric sulphate) is first heated without connection with the condensers till all the water has been driven out, and fumes of SO_2 and SO_3 appear, whereupon the connection is established and the heating continued. The residue in the retort is again treated with ordinary sulphuric acid, and thus used over and over again (comp. Neale's patent, *infra*).

Sometimes the acid from Bohemian vitriol stone is black and must be decolorized by the addition of a little nitric acid, which diminishes its value, since the nitric acid cannot be totally removed again.

The acid which is used in the manufacture of artificial alizarine must be still richer in anhydride than the best oleum as it formerly came from Bohemia. This so-called "*solid sulphuric acid*" the alizarine-manufacturers formerly made for themselves by heating the oleum in cast-iron retorts and receiving the escaping anhydride in another part of the acid, contained in iron vessels entirely protected from the access of air; but when greater demand for it arose, the Bohemian works laid themselves out for supplying fuming O.V. at all strengths, even up to *pure anhydride*.

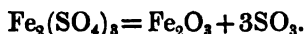
The production of sulphuric anhydride and fuming oil of vitriol from artificially prepared sulphates.

Two ways are possible for preparing SO_3 from sulphates, viz. either employing such sulphates which split up at a sufficiently low temperature, or employing those compounds which stand midway between SO_3 and the sulphates, that is, pyrosulphates of the type



The only representative of the former class is the *normal ferric sulphate*, $\text{Fe}_2(\text{SO}_4)_3$. It is true that many other sulphates can be decomposed by heat, as those of aluminium, zinc, copper, &c.; but in all cases except the first, the decomposition takes place only at temperatures at which SO_3 itself splits up into SO_2 and O. Thus for instance, the ZnSO_4 , so easily formed in roasting blende, on heating to a bright red-heat yields ZnO , SO_2 , and O, but no SO_3 .

But ferric sulphate is already decomposed at a dark red-heat, scarcely visible in daylight, so that the SO_3 given off is not yet decomposed, and the reaction is simply :



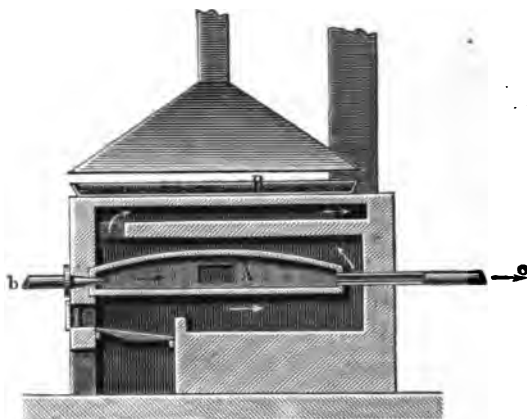
It is true that this reaction can never be realized to its full extent, as it is impossible to bring all the contents of the decomposing-apparatus exactly to the minimum temperature required ; a considerable portion of the mass is too much heated, and, moreover, much of the SO_3 first formed is subsequently over-heated in contact with hotter parts of the mixture or the walls of the apparatus, so that part of the SO_3 is always split up into SO_2 and O , and is thus lost, unless these gases are re-combined by special means, for instance as described above, p. 843.

Both this circumstance, and the difficulty of preparing ferric sulphate cheaply enough, have militated against the, apparently so easy, imitation of the Bohemian process, which consists in treating ferric oxide with strong sulphuric acid, heating the mixture till all the water has been driven off and dry ferric sulphate has been produced, and continuing the heating at a higher temperature, with condensation of the sulphuric anhydride evolved, the residue of ferric oxide serving over and over again for the same purpose. This process has not been found economical ; whether the modifications introduced by Schubert (p. 843) will effect this purpose remains to be seen.

It is, however, possible that the following process may be profitable, since under the special circumstances of the case the acid costs nothing (or less than nothing, considering the trouble caused by the necessity of removing it), and the value of fuel in the special local case is also extremely slight. Ragsosine and Dworkowitsch (G. P. 43,453) employ the acid tar produced in the purification of crude petroleum in enormous quantities and containing up to 90 per cent. free acid. This they mix with ferric oxide. On mixing there is a strong reaction, so that part of the water evaporates ; and sometimes even cooling is necessary, as the decomposition of the sulphate begins at 150°C . The solid mass produced is crushed and dried, and is heated to 300° or 500°C . Fig. 369 shows the furnace employed for this purpose. It consists of a muffle A with a very low arch ; through the tuyere *b* dry air is injected, and the heavy vapours of sulphuric anhydride are drawn

off through *c*. The waste fire-gases serve for drying the mass in pan B.

Fig. 369.



Some have proposed to employ copperas (ferrous sulphate), which, on calcination, yields basic ferric sulphate, $\text{Fe}_2\text{O}(\text{SO}_4)_{1/2}$; but this is evidently even much less promising than the process starting with Fe_2O_3 and H_2SO_4 , and the calculations made by Schemfil (French Patent, Dec. 2, 1869; *Monit. Scient.* 1870, p. 492) are entirely worthless.

Magnesium sulphate was patented by Sonstadt (March 3, 1875) in the shape of natural kieserite or calcined Epsom salts. The operation was to be carried out exactly as with ferric sulphate. But it is a fact (comp. Wagner's *Jahresb.* 1876, p. 327) that magnesium sulphate on calcination yields very little SO_3 , mostly SO_2 and O.

Sodium pyrosulphate, $\text{Na}_2\text{S}_2\text{O}_7$, is readily produced by heating the easily manufactured bisulphate, NaHSO_4 , till the chemically combined water is expelled. On heating to a higher temperature the pyrosulphate itself gives off sulphuric anhydride, $\text{Na}_2\text{S}_2\text{O}_7 = \text{Na}_2\text{SO}_4 + \text{SO}_3$, and the normal sodium sulphate left behind can be employed for again making bisulphate. This has formed the basis of more than one proposal.

Prelier (Engl. Patent, June 29th, 1847) has proposed to prepare fuming oil of vitriol by the following process, which is said to have been carried out in France on a large scale evidently only for a short time. 100 parts of calcined sodium sulphate are mixed with 2 parts of potassium sulphate and 2 parts of gypsum, charged into

retorts of sandstone (?), and a sufficient quantity of concentrated sulphuric acid added to form bisulphates. Then heat is applied; first all the water distils over, then sulphuric acid of 77° , then of 106° , then of 170° Tw., and at last fuming acid. The latter is known by the drops falling into water producing a hissing noise; then a receiver filled with acid of 170° Tw. is put on. This acid sometimes contains sodium sulphate. The residue in the retort is always used for the same purpose.

Wallace obtained an English patent (May 30, 1876) for heating sodium bisulphate in fireclay retorts; the formed anhydride or fuming vitriol is to be collected in earthenware jars with a lid perforated for receiving the gas-pipe, which can be replaced by a plain cover; thus the acid can be sent out in the receiver itself, and the fumes emitted in pouring it from one vessel into another are avoided. The fumes first coming over, which consist of aqueous sulphuric acid, are condensed separately. The sodium sulphate remains in the retort, and is always reconverted into bisulphate by adding sulphuric acid; so that continuous operation is possible.

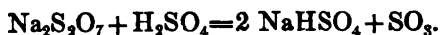
Fuming sulphuric acid from the action of boric acid upon sodium bisulphate (Kerl-Stohmann, 'Chemie,' 3rd ed. vi. p. 156).—This method has probably never emerged beyond the state of a suggestion.

From magnesium sulphate and sodium pyrosulphate mixed.—Wolters has obtained a German patent (No. 3110, March 5th, 1878) for this purpose. MgSO_4 acts upon $\text{Na}_2\text{S}_2\text{O}_7$ considerably below a red heat, a double salt ($\text{MgSO}_4, \text{Na}_2\text{SO}_4$) being formed and SO_3 being liberated. Instead of Na_2SO_4 , K_2SO_4 &c. may be employed. The remaining salt is reconverted into the mixture first employed by treatment with water and ordinary sulphuric acid, and exposing to sufficient heat. The value of this process is said to consist in the fact that the anhydride is liberated at a much lower temperature than from sodium pyrosulphate alone, thus preventing much loss, causing a larger yield of SO_3 , and permitting the use of ordinary fire-proof materials without any extraordinary wear and tear. (Experiments made in my laboratory with Wolters's process have to a great extent confirmed these statements.)

An additional German patent (No. 6091, Oct. 13, 1878) contains a simplification which I in my laboratory-experiments had employed as a matter of course. Instead of treating the residue from distillation with water and separating the salts by crystalliza-

tion, the dry double salt ($\text{Na—SO}_4\text{—Mg—SO}_4\text{—Na}$) is ground and treated directly with sulphuric acid (1 equivalent to 2 of salt, as otherwise half the acid passes over in the hydrated state).

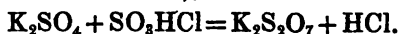
On the large scale Wolters's magnesium process does not seem to have been successful. But this appears to have been the case with a new process of his, patented in 1881 (G. P. 12,295). He prepares sodium pyrosulphate, in the usual manner, by heating the acid sulphate NaHSO_4 till the water has been expelled. When adding to the pyrosulphate a large quantity of monohydrated sulphuric acid there is a decomposition according to the formula :



The SO_3 is distilled off, and the hydrosodic sulphate is used for starting the process over again. This process is actually at work in several factories.

A further patent of Wolters's (G. P. 15,639) shows that on heating a mixture of a pyrosulphate with concentrated sulphuric acid in cast-iron vessels a crust of iron sulphide is formed, which firmly adheres and resists the acid in the process of distillation so long as the hydrosodic sulphate remains in the retort.

A detailed study of the pyrosulphates has been made by H. Schulze (Ber. d. deutsch. ch. Ges. xvii. 2705); we can give only a very short abstract here. Dry potassium or sodium sulphate absorbs SO_3 at the ordinary temperature with considerable evolution of heat; but if a complete potassium pyrosulphate is to be formed, a higher temperature is necessary (soaking with SO_3 and distilling off the excess at 100° to 120°). The sodium salt, treated in this manner, contains only 85 per cent. $\text{Na}_2\text{S}_2\text{O}_7$. Many other bases form pyrosulphates as well. The method of Berzelius for preparing pyrosulphates, by heating the hydrosulphates, gave unsatisfactory results; a better result is obtained by heating sulphates with chlorosulphonic acid (employing an excess of this, which is afterwards distilled off), the reaction being :



[Unfortunately chlorosulphonic acid has hitherto been prepared by means of SO_3 , so that that process is not available for technical purposes.]

An excellent process for preparing sodium pyrosulphate is that of Baum (G. P. 40,696). 240 kilog. hydrosodic sulphate, or else 142 neutral sodium sulphate, and 98 kgs. monohydrated sulphuric

acid are put into a cast-iron retort, provided with agitating-gear and connected with an air-pump. The latter is set in motion to produce a vacuum, and the retort is heated first to 260° , afterwards, with constant agitation for 5 to 8 hours, to 300° or 320° . Most of the water comes off between 260° and 280° , if the vacuum is equal to a column of 500 or 600 millim. mercury; the heating to 320° is only done to make quite sure of finishing the reaction. It is useful to place between the retort and the air-pump a cooler, connected by a glass tube with a receiver. When no more water is observed to run down the glass tube the reaction is finished, and the melted mass is poured out to solidify into plates consisting of pure $\text{Na}_2\text{S}_2\text{O}_7$ (comp. Schuberth's process, p. 842).

The Utilization of the Sulphuric Anhydride contained in Pyrites-kiln Gases.

It is well known that ordinary pyrites-kiln gases contain a somewhat considerable quantity of sulphuric anhydride which may occasionally amount to nearly 10 per cent. of the total sulphur acids present; and this quantity can be increased by prolonging the contact of the gases with red-hot ferric oxide, as shown in detail on p. 315 *et seq.* This fact has been utilized by various inventors. Majert and Messel (E. P. 1201, 1878) pass the burner-gas through concentrated sulphuric acid, which dissolves the SO_3 , and can thus be brought up to real monohydrate, H_2SO_4 , or even further; but undoubtedly this acid must be saturated with SO_3 as well, and this will make it useless for most purposes.

A process which seems to be actually carried out on a large scale consists in submitting the burner-gas to the catalytic action of finely-divided platinum (see below). In this case the previously present SO_3 is increased by that newly formed, so that the condensation becomes easier and more remunerative. But the burner-gas is thereby impoverished to a great extent, and rendered less fit for the manufacture of ordinary sulphuric acid in the lead-chambers.

Dehydration of Sulphuric Acid by Metaphosphoric Acid.

Nobel and Fehrenbach (E. P. 10,860, of 1884) pass the vapours of boiling strong sulphuric acid over lumps of metaphosphoric

acid heated to 320° . This acid retains the water and part of the sulphuric acid, whilst vapours of sulphuric anhydride are given off and are condensed in the usual manner. The operation is performed in a vessel of glass or platinum heated in a sand-bath, the sulphuric-acid vapours being passed in by a tube reaching nearly to the bottom. The vapours of SO_3 escape at the top, the liquefied mixture of phosphoric and sulphuric acid runs out of the bottom, and is reconverted into metaphosphoric acid by evaporation and calcination at a low red heat. [Hitherto no material was known in which this process could be carried out. Glass or platinum certainly do *not* resist the action of fused phosphoric acid for any length of time.]

The Preparation of Sulphuric Anhydride and Fuming Acid by Synthesis from Sulphurous Anhydride and Oxygen.

Without entering into the question how "catalytic" actions are to be scientifically explained, we will designate by this term the synthesis of SO_3 from SO_2 and O by the mediation of some third substance which remains unchanged at the end of the process, although it is more than probable that it undergoes some temporary change which is constantly undone again, so that in the end it cannot be traced with any certainty.

Phillips (who already on March 31st, 1831, had taken out an English patent for uniting SO_2 and O by ignited platinum &c.) and *Magnus* (*Poggendorff's 'Annalen,'* xxiv. p. 610) observed in 1832 that a mixture of 2 vols. of sulphurous acid and 1 vol. of oxygen gas, which in the dry state remains unchanged, is gradually condensed in the presence of water, but much more quickly in the presence of ignited platinum. If the moist mixture of SO_2 and O or atmospheric air is conducted through a darkly red-hot tube containing platinum sponge or wire, nearly all the SO_3 is condensed to oil of vitriol; dry platinum black converts the mixture into fuming acid (*Doebereiner, ib.* p. 609). *Magnus* even observed the formation of a little sulphuric acid on conducting the mixture through a darkly red-hot tube containing broken glass—and, in a smaller degree, through an empty tube; *Mahla* certainly could not confirm this. *Blondeau* (*Compt. Rend.* xxix. p. 405) found in 1849 that darkly red-hot argillaceous sand has the same effect upon a moist mixture of SO_2 and O.

The formation of *anhydride* under these circumstances had been

already noticed by Phillips and Magnus ; and Doebereiner's above-mentioned experiment had confirmed it. Woehler and Mahla found in 1852 (*Ann. Chem. Pharm.* lxxxi. p. 255) that the oxides of copper, iron, chromium, best of all a mixture of chromium and copper oxide, brought to a low red heat, caused the formation of thick fumes. Platinum as sponge and sheet did not act at ordinary temperatures ; but it acted far below red heat, copper sponge only after superficial oxidation. Woehler's results gave an impetus to several trials on the large scale (for instance, at the Oker works), which, however, remained fruitless (*Wagner's Jahresb.* for 1859, p. 144), because the time required for the reaction was too considerable. No more success was attained by Schneider's process, with platinized pumice, much praised in 1848 (*Dingler's Journ.* cvii. pp. 159, 363, cix. p. 354), and by the trials of Plattner (*Die metallurgischen Röstprocesse*, p. 339) and Reich (*Dingler's Journ.* ccxvii. p. 230), both the latter made at the Mulden works with ignited quartz as the catalytic substance. Exactly the same process has been again proposed by Piria ('*Cimento*,' ii. p. 293 ; *Liebig's 'Jahresb.'* 1859, p. 308), evidently only for laboratory use, as the sulphurous acid was to be made from sodium sulphite and dilute sulphuric acid ; and not atmospheric air, but oxygen was to be employed. Kuhlmann once more patented the same method in 1858 ; other patents, by Laming (1848), Robb (1853), Trueman (1854), Schmersahl and Bouck (1855), alike contain nothing new.

Most of these proposals were made with the object of replacing the lead-chamber process by one believed to be simpler and better, and did not aim at the production of sulphuric anhydride or fuming oil of vitriol, but of ordinary sulphuric acid. Thus, for instance, Phillips (see above) proposed to drive sulphurous acid, made by the combustion of sulphur, and mixed with an excess of atmospheric air, by means of a blowing engine through a nearly red-hot cast-iron tube filled with platinum sponge or finely rolled-up platinum wire ; the sulphuric acid vapour, formed therein, was introduced, along with the nitrogen and the atmospheric air present in excess, at the bottom of a long upright lead cylinder filled with pebbles, over which water continually trickled down for condensing the sulphuric acid. In order to save the expensive use of platinum alone, Piria proposed pumice impregnated with platinum salt and ignited ; and most of the other inventors enumerated above propose to do altogether without platinum. But all these attempts failed ;

the reaction was too slow and imperfect, and altogether incapable of competing with the ordinary lead-chamber process.

The matter takes a different aspect when the question is not that of competing with the lead-chamber process for ordinary vitriol, but with the Bohemian process for fuming acid, or for making sulphuric anhydride itself on a manufacturing scale. This latter had never been done till the most recent time; and the Nordhausen acid is made in Bohemia exactly in the same way as it was nearly a century ago, with an enormous expenditure of labour, fuel, space, and vessels, and on a very small scale, only enlarged by repetition of the apparatus. Although these circumstances and the fact of being dependent upon the occurrence of copperas-slates had gradually given a monopoly of the manufacture of fuming vitriol into the hands of that single Bohemian firm, its use has recently very much increased, since fuming acid is now employed for purifying some descriptions of mineral oils, for the manufacture of benzenedisulphonic acid, anthracenedisulphonic acid, and many other organic sulphonic acids serving as intermediate stages in the manufacture of colouring-matters. It could be predicted with certainty that this powerful chemical agent would acquire eminent technical importance as soon as the monopoly of its production was broken. It is the great merit of Professor Cl. A. Winkler to have brought this question to a focus in 1875 by a fundamental research (Dingler's Journal, ccxviii. p. 128; Wagner's Jahresb. 1875, p. 296), the contents of which I give in abstract, as follows:—

Winkler, in the first place, proposes to emancipate the manufacture of Nordhausen acid from local circumstances, such as the occurrence of copperas-slates, by making vitriol stone by the treatment of ground caput mortuum with concentrated oil of vitriol. These two bodies unite on gentle heating to a yellowish-white hard mass of ferric sulphate. The water of the sulphuric acid is evaporated by the heat developed in the reaction itself, without any external heat being applied, if quantities not too small are employed and the proper proportion of 1 part of caput mortuum to 1·8 part of acid is observed. If, instead of acid of 168° Tw., chamber-acid be used, the mixture of this with ferric oxide still hardens on prolonged heating to vitriol stone, the water being volatilized. The caput mortuum can be replaced by any other form of ferric oxide, such as burnt pyrites, if pure and very finely ground. The ferric oxide-

is always recovered again on distilling the oil of vitriol, and can be used over again for producing fresh vitriol stone.

The distillation of oleum, however, is a process little suited for working on a large scale. The bulky apparatus and the difficulty of managing it justly deter every one from trying to apply it elsewhere than where it has been practised of old. The manufacture of oleum can only become general if sulphuric anhydride is no longer produced by heating certain anhydrous sulphates, but directly from sulphurous acid and oxygen by catalytic action. The possibility of this had been proved long ago; and the principal difficulty was that of choosing the fittest substance for the contact action. This must in any case be platinum in a fine state of division; but, on account of its costliness, it must be spread over an indifferent surface, by which, also, its activity will be increased. Most highly to be recommended for this purpose is platinized asbestos, obtained by soaking soft, loosely felted asbestos with a concentrated solution of platinum chloride, then dipping it in a solution of sal-ammoniac, drying and igniting it. Much less efficient are other contact substances impregnated with platinum, such as pumice or porous earthenware.

The action of heated platinized asbestos upon a mixture of SO_2 and O may under certain circumstances lead to a very strong formation of anhydride; but it is not so in the presence of other diluting gases, as the following experiments show. The platinized asbestos was of a soft, woolly texture, and contained 8.5 per cent. of platinum. It was employed in a tube heated to a low red heat, in a layer 12 inches long and $\frac{1}{2}$ inch thick. The dried gaseous mixture entered at one end of the glass tube, passed over the asbestos in a moderately quick current, and at the other end was first conducted into water, then into a solution of sodium carbonate. Of 100 parts SO_2 employed, there were converted into SO_3 on the application of,

1st, a mixture of pure SO_2 and pure O	73.3 parts.
2nd, " " SO_2 and air	47.7 "
3rd, a gas with 4 per cent. SO_2 by volume, obtained by burning sulphur in a current of air	11.5 "

Thus the action of the platinized asbestos, and probably also that of all other contact substances, is lessened to the same extent as

the dilution of the sulphurous acid by indifferent gas increases; and an excess of sulphurous acid or oxygen beyond the stoichiometrical proportion of SO_2 and O must also be regarded as such *.

Now it is well known that the *ordinary strong sulphuric acid decomposes at a strong red heat into sulphurous acid, oxygen, and water*. Of these the water can be easily and completely condensed, and there remains a mixture of SO_2 and O exactly in the proportion necessary for forming SO_3 . In this way every admixture of indifferent gas could be avoided; and the SO_2 and O could be reunited by catalytic action, and thus the sulphuric hydrate be indirectly converted into anhydride. In order to carry this out experimentally, the following apparatus was constructed. A wrought-iron tube was covered inside and outside with a mixture of fireclay and waterglass; this was burnt in, the tube filled with bits of porcelain, and then brought to a strong red heat in a charcoal furnace. Into a cork at one end a bent funnel-tube was inserted, through which sulphuric acid of 170°Tw. was continuously dropped in; its supply was regulated by a Mariotte's bottle and a screw clamp. The sulphuric-acid vapour generated, passing through the red-hot tube filled with bits of porcelain, was decomposed, although not completely, into SO_2 , O, and H_2O . The latter was retained in a vessel filled with pumice soaked with strong sulphuric acid, together with the undecomposed sulphuric acid. The remaining dry mixture of SO_2 and O entered a long glass tube bent downwards at the further end, the horizontal part of which was filled with platinized asbestos, whilst the vertical branch entered a receiver filled with strong sulphuric acid. This was succeeded by a second similar receiver, and this by a receiver filled with a solution of sodium carbonate for the absorption of SO_2 . As soon as the platinized asbestos had, by means of a gas-furnace, been brought to a low red heat, an ample formation of sulphuric anhydride was observed, which partly condensed in a solid state in the tubes. The operation went on regularly, without any special supervision. After several hours the experiment was interrupted, and the contents of the first receiver were found entirely converted into fuming vitriol. It

* This part of Winkler's research has become obsolete through the invention of more active contact-substances, to which he has himself given the first impetus (see below). It is now possible to effect a far more complete combination of SO_2 and O, even when diluted with much N.

was ascertained that 93 per cent. of the sulphuric acid employed had been decomposed, and of the quantity decomposed 78 per cent. had been combined into SO_3 .

For carrying out this process on a large scale Winkler proposes the following apparatus :—The decomposition of the sulphuric acid is to take place in a furnace containing fireclay retorts, similar to gas-retorts, covered by brickwork at both ends. These are to be filled with large bits of quartz, fire-bricks, potsherds, &c., and carry the usual mouthpiece with a pipe for taking away the gas. At the other end a wrought-iron Welter's funnel tube is to be fixed. Through this, while the furnace is in full red heat, a continuous jet of strong sulphuric acid is run in, and in the red-hot retort is immediately vaporized and decomposed. Perhaps upright retorts would answer the purpose still better. [Very probably it would be preferable to evaporate the sulphuric acid in separate vessels.] The mixture of SO_2 , O, and aqueous vapour thus obtained in a constant stream is conveyed from the different retorts into a main tube serving as receiver, and passes from this into the condenser, in which the greater part of the water as well as the sulphuric acid carried away is condensed. The condenser would suitably consist of a system of lead pipes, cooled by air or water, similar to the condensers at gas-works. The sulphuric acid running away from it, and perhaps showing 22° to 33° Tw., which must be strongly charged with sulphurous acid, would be returned to the chamber-process. The gaseous mixture is then dried in one or, if necessary, in two coke-towers, by a spray of sulphuric acid of 144° Tw. It can now be exposed to the action of the ignited asbestos, of which 50 to 100 kilog., containing 4 to 8 kilog. platinum, would suffice for a pretty large manufacture. A diminution of the contact-action, which it has been feared might take place in time, could only be caused by ashes, dust, soot, &c., none of which can come into action here; besides, the platinum, if necessary, could easily and cheaply be extracted and transferred to fresh asbestos. The action of the platinized asbestos on the mixture of SO_2 and O begins at a scarcely visible red heat; and therefore, on the large scale, the heat of the fire-gas escaping from the furnace for decomposing the sulphuric acid will be available for this purpose. The fire-gas is conducted through a muffle-shaped chamber built upon the first furnace, in which several fireclay pipes, glazed with a porcelain enamel, are placed, loosely filled with platinized

asbestos. The gas enters this after leaving the drying-tower; the sulphuric anhydride formed is conveyed away by similarly glazed stoneware pipes, and either condensed as such or dissolved in ordinary strong vitriol. If the latter has to be done, the vapours of the anhydride are allowed to enter a tower fitted with ridges of lead jagged out at the bottom, over which a steady shower of strong vitriol trickles down; the supply of the latter is so regulated that the acid leaves the tower in the fuming state, and can at once be filled into carboys. Possibly this last operation requires the combined action of several towers, in which case they are best placed one on the top of another, so that the acid can run from one to the other and become gradually saturated. Even if on the large scale the union of SO_2 and O should not take place completely, the remainder of the gaseous mixture can be introduced into ordinary vitriol-chambers, and here condensed in the usual manner by itself.

Winkler adds the remark that the mixture of SO_2 and O may be just as well generated by strongly heating vitriol stone or other anhydrous sulphates in large vessels, such as the retorts employed in zinc-making, and transformed, by means of platinized asbestos, into sulphuric anhydride. Then the solid residue would certainly have to be dealt with; but, on the other hand, the drying of the gas would be saved, and at all events the drawbacks of the present manufacture of oleum would be avoided. [A proposal quite similar to this (certainly the least essential) part of Winkler's process was made by Prelier in 1847 (see p. 846).]

At the same time as Winkler, and quite independently of him, Squire and Messel conceived the idea of combining these two well-known reactions, the splitting up of sulphuric acid by heat into H_2O , SO_2 , and O , and the recombination of SO_2 and O by finely-divided platinum. Their patent dates from Sept. 18, 1875, and was published in March 1876, whilst Winkler's research, which was of course not merely made, but even written out some time before, appeared in the October number of 'Dingler's Journal' of 1875. The coincidence between Squire and Messel's patent and Winkler's proposals is certainly remarkable, but there cannot be the slightest doubt that they hit independently upon the same ideas, which were "floating in the air" at that time. There is, however, one important difference. Squire and Messel still proposed, like so many of their predecessors, platinized

pumice, whilst Winkler showed that asbestos is far superior to pumice or any other material for finely dividing the platinum and giving it the greatest possible surface of contact. Whilst probably (so far as can be known in face of the strict secrecy observed in this branch of industry) no other part of their proposals (more especially the preparation of SO_2 and O by decomposing H_2SO_4) is now carried out exactly as originally put forward by Squire, Messel, and Winkler, Winkler's proposal of employing platinized asbestos as "contact substance" seems to have been universally accepted.

In a later publication (Dingl. Journ. ccxxiii. p. 409) Winkler mentions that Debray ('Les Mondes,' 1876, No. 3) had objected to his process that it was not suited to the manufacture of Nordhausen acid on the large scale, on account of the great difficulty of decomposing the sulphuric acid at a high temperature, and of the rapid destruction of the vessels. Neither metal nor earthenware vessels resist the sulphuric-acid vapours at such temperatures; and even platinum is permeable to gases at such a heat, and would be much damaged by the action of the flame and the impurities of the sulphuric acid. To these objections Winkler replies that he had decomposed his sulphuric acid in iron tubes without any difficulty, and that even earthenware vessels can be used, if the sulphuric acid is not allowed to run into the red-hot retort itself, but on to a porous layer of alumina or ferric oxide, in which it is absorbed in order to be at once vaporized again. Debray himself mentions that in the laboratory of the École Normale at Paris 3 kilog. of sulphuric acid per hour were decomposed in a platinum tube of 120 centims. length and 25 centims. diameter, without mentioning whether this was filled with bits of porcelain or bricks. In a decomposing-vessel of the size of a gas-retort at least five times as much, say 15 kilogs. per hour, could be decomposed—therefore, in a furnace with five retorts, 75 kilogs. per hour, or 1800 kilogs. (=36 cwt.) daily, which, at the rate of 75 per cent. of anhydride, would amount to a yield of 1000 kilogs. of the latter, or, by dissolving it in strong vitriol, of 2500 kilogs. (=2½ tons) Nordhausen acid. Four such furnaces would be able to cover the whole quantity of 3000 tons Nordhausen acid made at that time per annum. Winkler also considers it remarkable that Debray should make the above objections, since he and Deville in 1861 had recommended the decomposition of sulphuric acid as the cheapest source of oxygen, and several others had followed them; their process, as is

well known, was exhibited in a special laboratory at the Paris Exhibition of 1867, but certainly was discontinued directly after. Winkler complains that, if Debray had found his own rather too confidently-made statements to be erroneous, he should have corrected them himself. [Such things do happen elsewhere as well!]

As far as can be learned from practice, it is just the two difficulties mentioned by Debray which militate against the process, especially the decomposition of the sulphuric acid. The greatest difficulty in Winkler's process for manufacturing fuming oil of vitriol or anhydride, and in all other processes started in consequence of the impetus given by him, is indeed the material of the vessels to be employed. Wallace, in his above-mentioned patent, proposes to employ glazed plumbago retorts. Some actually working factories seem to employ platinum vessels, which certainly are strongly acted upon, as was shown by Scheurer-Kestner (see above). The extent of this action will partly depend upon the amount of arsenic and nitrous acid contained in the sulphuric acid (comp. Wagner's 'Jahresbericht,' 1877, p. 238), partly also upon the special construction of the apparatus. According to communications received direct by me from Dr. Majert, the apparatus employed by him at the Schlebusch works, near Cologne, was arranged as follows:—The decomposition of sulphuric acid into SO_2 , O , and H_2O was effected in upright retorts made of a mixture of 3 parts burnt fire-clay broken to the size of a pea, and 1 part best Belgian fire-clay, and glazed with a mass which at the highest temperature of the process becomes pasty but not liquid, so that any cracks occurring in the retort fill themselves up with the glaze. The retorts are perpendicular, entirely surrounded by the fire, and closed at top and bottom by hydraulic joints. The top joint serves for introducing the pipe conveying the acid to be decomposed, the bottom joint for making the sides of the retort tight in the fixed bottom, which is perforated by the pipe which carries off the gases. Both the "hydraulic" joints, which are entirely surrounded by the fire, are luted with melted glass. Within the first retort there is a cylinder, into which the vitriol flows from a small platinum tube, so as not to touch the sides of the retort at all. It is thus evaporated within the inner cylinder, and is partly decomposed there, partly in the annular space between the cylinder and the retort, and completely in the

second retort. The vapour and gases are conveyed from the first to the second retort by a twice-bent tube, which passes through the bottoms of both retorts, and whose horizontal part is surrounded by the flame of the fireplace. The gases pass away from the top of the second retort into a condenser for liquefying most of the water, then into a drying-tower, and at last into the apparatus for uniting SO_2 and O , consisting of cast-iron retorts filled with wire-gauze shelves, upon which the platinized asbestos is spread. (This factory has not been at work for a long time.)

Angerstein (G. P. 26,959) describes a special apparatus for decomposing the sulphuric acid, which is supplied from below, is evaporated in a shallow platinum dish, and decomposed in fire-clay pipes filled with broken fire-bricks, and heated outside to a very high temperature by the combustion of gaseous fuel under pressure.

According to a German patent of Squire's (No. 4285, March 3, 1878), strong vitriol is introduced into a red-hot tower packed with hollow bricks and previously filled with dry steam. The vitriol is in the form of a mist, produced by a compressed gaseous mixture of sulphurous acid and oxygen. The products of decomposition are conveyed in a horizontal closed channel through a lead pan filled with dilute sulphuric acid, where the water is condensed by cooling, whilst the heat of the gases concentrates the sulphuric acid contained in the pan and frees it from sulphurous acid. A further condensation takes place in cooling-pipes; and ultimately the gases are dried in a coke-tower by means of strong sulphuric acid, which is again concentrated and freed from SO_2 in the lead pan just mentioned. The dry mixture of SO_2 and O is combined into SO_3 in a specially heated apparatus of cast iron outside and brickwork inside, fitted with a pyrometer, where it is brought into contact with platinized asbestos, being forced to travel a circuitous path between courses of bricks. The vapour of anhydride is absorbed by strongest vitriol in a cast-iron tower, fitted with dishes of a peculiar shape, placed one on the top of another. (The specification gives further details and diagrams of the apparatus.)

It would seem as if the decomposition of sulphuric acid by heat, for the purpose of obtaining a suitable mixture of SO_2 and O , had been given up everywhere, owing to the great expense of the process and the extreme wear and tear of the apparatus.

Ordinary pyrites-burner gases are probably in many cases the material from which sulphuric anhydride is made (comp. p. 849), and this, no doubt, always by means of asbestos platinized in some shape or another. No doubt both the apparatus and the details of the processes differ very much in different works, but nothing is publicly known about it, and we must confine ourselves to giving abstracts from the various patents taken out.

Rath (G. P. 22,118) passes pyrites-burner gases, to free them from most of the water, through a cooling-apparatus, consisting of a large number of perpendicular lead pipes placed in cold water, at a velocity not exceeding 5 inches in the second. Air may be admitted to them by means of a valve. From the cooler the gases pass through a coke-tower fed with acid of 140° Tw. In order to be thoroughly dried here, the velocity of the gaseous current should not exceed $2\frac{1}{2}$ inches. From here the gases are aspirated by a pump and forced through a number of iron retorts, lined with clay, which contain the contact substance, and are heated to a temperature between dark and bright red heat. The number and size of these retorts must be chosen in such manner that the velocity of the gases does not exceed $2\frac{1}{2}$ inches. The sulphuric anhydride formed here is either condensed in the liquid form in tin-plate vessels standing in a place heated to 25° to 30°, or else it is passed into cast-iron vessels charged with sulphuric hydrate and kept at 25°. Special precautions are required for gases containing carbon monoxide or hydrocarbons.

J. Neale (English patent of March 14th, 1876) heats anhydrous sulphates or bisulphates of iron, zinc, aluminium, or sodium in earthenware retorts or muffles, and conducts the mixture of sulphurous acid and oxygen formed by their decomposition over heated spongy platinum, or the oxides of chromium, iron, or copper, or any other substance which may cause the mixture to combine into sulphuric anhydride. The latter is then condensed by itself or utilized for fuming oil of vitriol by receiving it into ordinary strong sulphuric acid.

Scheurer-Kestner (Compt. rend. 99,876) asserts that on heating a mixture of 2 parts of anhydrous calcium or magnesium sulphate with 1 part of ferric oxide to a bright red heat, all the sulphuric anhydride is driven off, at first as such, afterwards decomposed into SO₂ and O. By mixing 175 parts of gypsum with 100 of fluor-spar and ferric oxide, the decomposition takes place at a

lower temperature (that of the Bunsen burner) and the SO_3 is then not dissociated into SO_2 and O .

Undoubtedly the combination of SO_2 and O by contact with platinum is greatly promoted by employing either both or at least one of these gases in a pure form. Since pure sulphur dioxide, free from any gaseous admixtures, can be easily prepared by the process of Haensch and Schroeder (p. 289), this task is very much facilitated. These chemists themselves operate in the following manner, which has been found entirely successful on a manufacturing scale (G. P. 42,215 ; E. P. 9188, 1887) :—A mixture of pure sulphur dioxide and air in a certain fixed proportion is passed at a low red heat, and under pressure, over platinized asbestos, whereby a large surface and a lengthened duration of contact is ensured to the gases. The pressure also promotes chemical reaction by bringing nearer together the active gas molecules. A gas-mixture consisting of 25 per cent. SO_2 and 75 per cent. air is most suitable for the process ; the mixing of the gases simultaneously with their compression is effected by a double cylinder compressor, the two cylinders of which have a cross sectional area in the proportion of 1 : 3, so that one cylinder pumps three times as much air as the other pumps sulphurous anhydride. The compressed gases meet in the conducting-tube and pass into an air-chamber, and thence into the combining-apparatus. This consists of two horizontal wrought-iron tubes, set in a furnace, of somewhat narrow diameter and strong walls, sufficient to stand a pressure of several atmospheres at a dark red heat ; they are filled with platinized asbestos prepared in a special manner. The pressure (usually 2 to 3 atmospheres) is regulated by a valve at the common exit-tube. Here most of the SO_3 is converted into SO_2 , and lest this should deposit in a solid form in the tubes or in the valve, the parts projecting from the furnace are surrounded by a leaden steam-coil. If in spite of this there should be some obstruction by the crystallization of SO_3 , the pressure in the air-chamber will raise a valve, weighted about 1 atmosphere, above the exit-valve. From the latter the remaining gases pass through condensing jars, where the SO_3 deposits in the solid form, or is retained by strong sulphuric acid. The SO_2 still present is separated from the nitrogen by water, and used over again. [This process is carried out at several large factories, and is probably the most successful of all those working at present.]

Nitrogen would be entirely excluded by the employment of oxygen as first proposed by Messel (E. P., Jan. 15, 1878). He prescribes burning sulphur by means of oxygen, obtained by the electrolysis of acidulated water with the help of dynamo-electrical machines. The sulphurous acid formed, mixed with the excess of oxygen required for forming SO_3 , is conveyed into a gas-holder, from which the gases are carried at a high temperature over spongy platinum, platinized asbestos, oxide of chromium, iron, or copper. The anhydride formed is condensed by itself or absorbed in sulphuric acid. By employing two gas-holders the process is made continuous. The electrolytical hydrogen formed at the same time is employed for heating, or it is carburetted and employed for lighting. This process must have been too expensive, owing to the cost of electrolytically-made oxygen. When that gas became a cheap commodity through the development of Brin's processes, I myself (Ellice-Clark's patent, No. 3166, 1888) proposed utilizing such oxygen in a similar manner, in such way that no external heat should be required, and there should be no waste gases of any sort. I abstain from giving a detailed description or drawing of the apparatus proposed by me, as it seems proved that the admixture of nitrogen does not, as formerly assumed, prevent a complete oxidation of SO_2 , at least when the latter is present in a concentrated form, provided the contact substance is sufficiently active; this circumstance robs the pure oxygen of its advantages in comparison with atmospheric air.

O. von Gruber (G. P. 27,726) proposes making SO_3 from nitrososulphuric acid (chamber-crystals) by heating them with dry air and sulphurous anhydride at a higher temperature, and recovering the nitre gas evolved.

Acid tar, as obtained in the chemical treatment of petroleum, paraffin, and the like, is utilized for the manufacture of SO_3 by J. D. Starck (E. P. 12,028, 1889) in the following manner, which differs from the process of Ragsone and Dvorkowitch (*vide supra*, p. 845) by the employment of Winkler's reaction and otherwise:—The acid-waste is fed in at the lower end of an inclined iron retort, within which revolves an endless screw, for the purpose of drawing outwards the residual coke-like mass. The sulphurous anhydride and water produced are freed from water and hydrocarbons by means of a condenser and wash-chamber; they are then dried in a sulphuric-acid tower, mixed with a suitable proportion of dry

air or oxygen, and conducted through a tube containing platinized asbestos or other contact-substance. The SO_3 produced is condensed or absorbed in sulphuric acid, and the residual SO_2 is passed into ordinary vitriol chambers.

Recovery of sulphuric anhydride from waste materials containing such, as obtained in the manufacture of coal-tar colours. This is the object of a proposal of *Schulze-Berge* (G. P. 35,620), who employs a partial vacuum for distilling SO_3 from such mixtures by means of a special apparatus.

Improvements in the Manufacture of Contact-Substances.

A German patent of Cl. Winkler's (No. 4566, Sept. 21, 1878) describes the preparation of extremely active catalytical substances from precious metals or metallic oxides in the finest state of division, with which an indifferent porous matter is impregnated almost in the same way as a textile fabric is dyed in the beck. The best catalytical substance is platinum, also iridium or palladium, less so the oxides of iron, chromium, manganese, cobalt, and copper. As an indifferent menstruum almost any loose porous body may be used, preferably asbestos, but also glass-wool, pumice, infusorial earth (Kieselguhr), clay, and where a very high temperature is not required, even cellulose, cotton wool, gun-cotton, sponges, &c.

In order to charge asbestos with finely divided platinum, it is thoroughly soaked with a solution of platinum chloride made alkaline by soda and mixed with sufficient sodium formiate to reduce the platinum. The well-wrought pasty mixture is dried in a water-bath; thus the platinum is separated as "platinum-black," and is firmly precipitated upon the fibre. The salts are removed by washing, without washing off the platinum. The quantity of the latter precipitated depends upon the strength of the solution of platinum chlorides; with asbestos or cotton-wool a percentage of 80 platinum may be attained. Metallic oxides exhibit catalytical action only at higher temperatures, and, accordingly, must be precipitated upon fire-proof substances. Thus asbestos or pumice may be thoroughly impregnated with chromium oxide by soaking in mercurous nitrate, then in ammonium chromate, drying each time, and ultimately gently igniting. Cupric oxide is precipitated firmly by soaking in an ammoniacal solution of cupric carbonate and gently igniting. Asbestos may also be

soaked with solutions of manganous or cobaltous chloride, &c., dried, put into a heated solution of bleaching-powder or of another precipitant, dried again, washed, and ignited. The contact-substances prepared in this wise, owing to their homogeneous condition and their very large surface, cause, either at the ordinary or at a higher temperature, the combination of certain gases, such as that of SO_2 and O into SO_3 , the conversion of the CS_2 in coal-gas into H_2S , the oxidation of the vapour of alcohol, &c. They may be employed for all reactions based upon the phenomena of so-called "catalytic action."

The preparation of extremely active platinum-black has been described by Loew ('Ber. d. deutsch. chem. Ges.' 1890, p. 289). Already Doebereiner has shown that the degree of activity of platinum-black differs very much with the method of preparation employed. That made with zinc and hydrochloric acid is less active than that made with an alkaline solution of glucose, and this is inferior to that which is precipitated from platinic sulphate by alcohol. The proportion is 1 : 1.8 : 2.6. Far more active again is the following preparation, made with formaldehyde of 40 or 45 per cent., which now forms an article of trade*. 50 grms. platinic chloride are dissolved in a little water, to a volume of 50 or 60 c. c., and mixed with 70 c. c. of 40 to 45 per cent. formaldehyde. To this is added, quite gradually and with good cooling, a solution of 50 grms. caustic soda in the same quantity of water. Most of the metal is separated at once. When, after 12 hours, the mass is filtered by means of a filter-pump, a yellow solution passes through, which on boiling separates a little metal. When, however, most of the salts (sodium chloride and formiate) has been removed by washing, a deeply black solution runs off, some of the black mud going into solution. Therefore the washing is interrupted until an oxidizing process now going on in the black mud has been finished, whereupon the liquor runs off colourless. That process consists in the rapid absorption of oxygen by the black mass on the filter; the temperature rises to 36° or 40° , and many gas-bubbles are given off with a crackling noise, lasting for several hours. The fine mud has now turned into a loose porous mass, which is washed till every trace of chlorides has been removed, then pressed and dried over sulphuric acid. Even a trace of sodium chloride is extremely prejudicial to the action of the

* It was sold, in 1890, at the price of 8 marks per kilog. by Merklin and Lüsskann, at Seelze near Hanover.

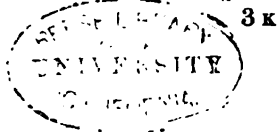
platinum-black, a coating of platinous chloride being formed in that case. The black mass evidently contains an organic compound of platinum, which is afterwards destroyed by oxidation.

Application of electricity for manufacturing sulphuric anhydride.—Leon (F. P. 206,088, June 9, 1890) proposes manufacturing sulphur trioxide by the electrolysis of sulphuric acid of 66° or 65°·5 Baumé. The current must not exceed $\frac{1}{10}$ ampère per square centimetre, in order to avoid heating. Thus SO_3 , H, and O are produced; the former is condensed and the latter escape. The electrodes are made of platinum or carbon; they are kept 2 or 3 millimetres apart by means of asbestos or glass-wool, which reduces the electrical resistance of the bath to 2 or 3 ohms per centimetre, and permits a near approach to the theoretical yield, viz. 1 kilog. H_2SO_4 for each half horse-power per hour, or 1 kilog. of 45 per cent. Nordhausen acid. Sometimes a deposit of sulphur is formed on the cathode, but this is got rid of by reversing the current.

Analysis of Nordhausen Oil of Vitriol.

Several communications have been made on this matter, as by Fürstenau (Chemiker-Zeitung, 1880, p. 18), Möller (ibid. p. 569), Becker (ibid. p. 600), Winkler (Chem. Ind. 1880, p. 194), Clar and Gaier (ibid. 1881, p. 251). We shall, however, principally describe the methods contained in Lunge and Hurter's 'Alkali-Maker's Hand-book,' as derived from practical information, with a few improvements.

In the present case even the *taking of the sample* is not quite a simple task. Measuring it in a pipette is out of the question, it must be weighed. But even for this purpose the article, if solid, must be first liquefied. This is comparatively easy with partly crystallized acid or with solid pyrosulphuric acid; these can be liquefied without any danger in a closed vessel by gently heating to 30° in a sand-bath. Soldered-up tins are generally placed in a suitably heated stove. There is no sensible loss of strength, if the aperture for this purpose is previously opened, and at once covered with a watch-glass. This prevents any pressure within the vessel during the heating, which must otherwise be guarded against in opening it. The case is different with products containing a larger percentage of anhydride. These do not liquefy completely, a por-



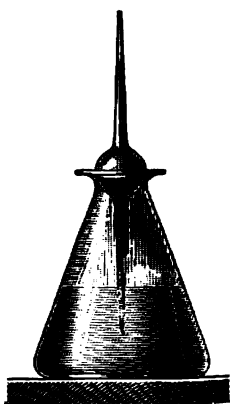
tion always remaining in the state of a gelatinous residue. This residue is, however, composed exactly like the liquid portion, so that the sample may be taken out of the latter without any danger of making a mistake.

The sample is weighed either in glass bulbs, or in a glass tap-tube. The former are very thin bulbs of about $\frac{1}{4}$ inch diameter, ending each way in a capillary tube (fig. 370). The liquefied acid (2 or 3 grams) is sucked into the bulb, without danger to the operator, by means of a bottle closed with an india-rubber cork, through which passes a tightly-fitting glass tap, connected at its free end with an elastic tube. Suction is applied to the latter, the tap is closed, the elastic tube is drawn over one of the capillary ends of the weighing-bulb, and by opening the tap a sufficient quantity of acid is admitted into the bulb.

The capillary tube is cleaned and one of the two ends is sealed at the lamp. The other end can be left open without fear of any loss of SO_3 or attraction of moisture during weighing. The weighing is best done on a small platinum crucible with two nicks, on which the ends of the bulb can rest. If the latter should be accidentally broken, the acid runs into the crucible, not on the balance. Then the bulb, open end downwards, is put into a small Erlenmeyer flask, into the neck of which it ought to fit exactly (fig. 370), and which contains so much water that the capillary tube dips pretty far into it to prevent any loss of SO_3 on mixing the acid with water. Now break off the other point, allow the acid to run out, squirt a few drops of water into the upper capillary, and ultimately rinse the whole bulb-tube by repeated aspiration of water. Dilute the liquid to 500 c. c. and take 50 c. c. for each test. The testing is done with fifth-normal solution of soda (1 c. c. = 0.008 grm. SO_3) and litmus or methyl-orange as indicator. The acidity found is diminished by that proceeding from SO_2 , found by titrating another sample with iodine.

In lieu of the bulb-tube (first proposed by Clar and Gaier) we prefer the glass tap-tube, as shown in fig. 371. The tap should be tight without greasing, and the tube below it should taper gradu-

Fig. 370.



ally. It is charged by suction, in the same way as described above, with about 0.5 gm. of Nordhausen acid, no more, in order to be able to titrate it directly, without taking an aliquot portion. After the proper quantity of acid has been introduced, the tap is closed, the tube is cleaned outside with filtering-paper, and it may be weighed at once, without any fear of a change of weight during the operation. It is, however, preferable to employ a tube (as shown in the cut) ground into an outer glass case, which is, of course, tared together with the empty tube.

After weighing, place the tube point downwards in water, or in

Fig. 371.



Fig. 372.



the case of nearly pure anhydride or the strongest Nordhausen acids in a layer of crystallized, coarsely powdered Glauber's salts,

and slowly run out the contents. Then squirt a drop of water from above into the tube, allow it to stand for a moment, and rinse thoroughly with water. Anhydride once melted for the purpose of filling the tube remains liquid enough to complete the weighing and running out without requiring to be heated again.

The most convenient apparatus for weighing off fuming sulphuric acid (as well as other fuming acids or substances evolving vapours) is undoubtedly the "bulb-tap pipette," proposed by Lunge and Rey (*Zeitsch. f. angew. Chem.* 1891, p. 165), and shown in fig. 372, in which both the filling as well as the weighing and discharging are performed without any loss of vapours, and without requiring any special aspirating-apparatus. Above tap *a* there is a bulb *b*, rather less than an inch in diameter, and above it a second tap *c*. The lower portion of the pipette is ground into a glass tube *d*, closed at the bottom. In the conical part of the pipette there is a rill *e*, reaching halfway down, the corresponding half of the rill *f* being in the outer tube. By turning the pipette in the latter, the tube *d* can be made to communicate with the outer air or the reverse. When the pipette is to be used, close tap *a*, suck at the top with the mouth, and before leaving off shut tap *c*, so that the bulb *b* contains a partial vacuum. Dip the point of the pipette into the acid and open *a*; the acid will rise up, but *a* is shut before it gets so far, or even sooner, when enough has got in. Clean the pipette outside, put it into *d*, and weigh. In most ordinary cases (with other acids, ammonia, &c.) the rills *e* and *f* are made to communicate; water is squirted through *c* into *b* and then run through *a*, with the contents of the pipette, into *d*, the air escaping through *e* and *f*. The dilute acid is run into a beaker and titrated. In the case of Nordhausen acid it is preferable to take the pipette out of *d*, rinse the latter into a beaker, run the contents of the pipette, by opening *a*, into water or Glauber's salt contained in the same beaker, then squirt water through *c* (during which time *a* may be closed), and rinse the pipette into the same beaker. The sucking at *c* is quite sufficient to produce the necessary rarefaction of air in *b*, and no vapours are lost, as is inevitable with any other kind of aspiration.

The sampling of solid sulphuric anhydride is not an easy matter. This substance, which is now a regular article of trade and is sent out in iron bottles, is much too compact and tough to enable a sample to be taken out by means of an auger. Before using it, it

is always heated in a stove till it has completely liquefied ; but in this state the bottle on opening emits such a dense cloud of fumes that any sampling is out of the question. The way out of the difficulty is this :—In a stoppered bottle some lumps of the solid anhydride are weighed off on a large balance and are then mixed with a sufficient quantity of accurately analysed monohydrated sulphuric acid (p. 738), to form an acid of 70 per cent. SO_3 , which is liquid at ordinary temperatures. The solution is promoted by gently heating the bottles, say to 30° or 40°C. , with the stopper loosely put on. At last a sample is taken out by means of the pipette described above (p. 868) and the analysis performed in the usual way, taking account of the slight proportion of water present in the “monohydrate” employed.

Setlik (Chemiker-Zeitung, 1889, p. 1670) proposes to substitute the following method for the titration of Nordhausen acid by caustic-soda solution :—50 or 100 grms. are weighed out in a long-necked flask, and water is dropped in very slowly from a burette, divided into $\frac{1}{10}$ c. c., till the fuming has ceased. During the operation the flask must be well cooled. In order to observe the finishing point, in the end the flask must be agitated after adding each drop till the fumes have been entirely absorbed by the acid. When no fumes whatever are formed at the surface and a drop, falling into the middle of the acid, dissolves quietly, the end is reached. Acid of more than 35 per cent. SO_3 must be previously diluted with monohydrated sulphuric acid. It is claimed that this plan is much more expeditious and quite as exact as the alkalimetric way ; but the analytical proofs adduced by Setlik himself do not bear this out (there are deviations up to 0.9 per cent. SO_3), and we can consider his method only as a test for internal use, but not between buyer and seller.

The results of titration are first calculated for the total (combined and uncombined with water) SO_3 , each c. c. of normal soda solution indicating 0.040 grm. SO_3 , and the proportion of free SO_3 and H_2SO_4 present is then read off by means of the following table (calculated by R. Guehm) :—

Found by titration, total SO ₃ .	The acid contains per cent.		Found by titration, total SO ₃ .	The acid contains per cent.		Found by titration, total SO ₃ .	The acid contains per cent.	
	SO ₄ H ₂	SO ₃		SO ₄ H ₂	SO ₃		SO ₄ H ₂	SO ₃
81-6326	100	0	87-8775	66	34	94-1224	32	68
81-8163	99	1	88-0612	65	35	94-3061	31	69
82-0000	98	2	88-2448	64	36	94-4897	30	70
82-1836	97	3	88-4285	63	37	94-6734	29	71
82-3674	96	4	88-6122	62	38	94-8571	28	72
82-5510	95	5	88-7959	61	39	95-0408	27	73
82-7346	94	6	88-9795	60	40	95-2244	26	74
82-9183	93	7	89-1632	59	41	95-4081	25	75
83-1020	92	8	89-3469	58	42	95-5918	24	76
83-2857	91	9	89-5306	57	43	95-7755	23	77
83-4693	90	10	89-7142	56	44	95-9591	22	78
83-6530	89	11	89-8979	55	45	96-1428	21	79
83-8367	88	12	90-0816	54	46	96-3265	20	80
84-0204	87	13	90-2653	53	47	96-5102	19	81
84-2040	86	14	90-4489	52	48	96-6938	18	82
84-3877	85	15	90-6326	51	49	96-8775	17	83
84-5714	84	16	90-8163	50	50	97-0612	16	84
84-7551	83	17	91-0000	49	51	97-2448	15	85
84-9387	82	18	91-1836	48	52	97-4285	14	86
85-1224	81	19	91-3673	47	53	97-6122	13	87
85-3061	80	20	91-5510	46	54	97-7959	12	88
85-4897	79	21	91-7346	45	55	97-9795	11	89
85-6734	78	22	91-9183	44	56	98-1632	10	90
85-8571	77	23	92-1020	43	57	98-3469	9	91
86-0408	76	24	92-2857	42	58	98-5306	8	92
86-2244	75	25	92-4693	41	59	98-7142	7	93
86-4081	74	26	92-6530	40	60	98-8979	6	94
86-5918	73	27	92-8367	39	61	99-0816	5	95
86-7755	72	28	93-0204	38	62	99-2653	4	96
86-9591	71	29	93-2040	37	63	99-4489	3	97
87-1428	70	30	93-3877	36	64	99-6326	2	98
87-3265	69	31	93-5714	35	65	99-8163	1	99
87-5102	68	32	93-7551	34	66	100	0	100
87-6938	67	33	93-9387	33	67			

or else by the general formula : $SO_3 = S - 4.444(100 - S)$, in which SO_3 means the free sulphur trioxide, and S the total SO_3 as found by titration.

This table serves also for the frequently performed operation of mixing Nordhausen acid of a certain percentage of SO_3 with concentrated sulphuric acid in order to produce an acid with a smaller percentage of SO_3 . This can be done by means of a formula given by Gerster (Chem. Zeit. 1887, p. 3),

$$x = 100 \frac{b-a}{a-c},$$

where x represents the quantity of sulphuric acid which must be

added to 100 parts of the Nordhausen acid; a the total sulphur trioxide in 100 parts of the acid desired; b the total SO_3 in 100 parts of the Nordhausen acid to be diluted; c the total SO_3 in 100 parts of the ordinary acid to be used for diluting. The values of a and b are taken from the preceding table; c is easily calculated by multiplying the percentage of H_2SO_4 with $\frac{80}{98}$ or 0.816. An

example will make this clearer. Supposing there is a Nordhausen acid of 25.5 per cent. SO_3 in stock, as well as sulphuric acid of 98.2 per cent. H_2SO_4 , and an acid of 19 per cent. SO_3 is required, we have then:

$$a = 85.1; \quad b = 86.3; \quad c = 98 \times 0.816 = 80.1,$$

$$x = 100 \frac{b - a}{a - c} = 100 \frac{86.3 - 85.1}{85.1 - 80.1} = \frac{120}{5} = 24.$$

That is: by mixing 100 parts of acid of 25.5 per cent. SO_3 with 24 parts of sulphuric acid of 98.2 per cent. H_2SO_4 , Nordhausen acid is obtained containing 19 per cent. SO_3 . [In reality the strength of the mixed product will be slightly below that calculated, as a certain loss of SO_3 is hardly avoidable in the manipulation.]

Nordhausen acid is always sold by the percentage of uncombined sulphuric anhydride it contains (not taking any account of the pyrosulphuric acid, which is considered $= \text{SO}_3 + \text{H}_2\text{SO}_4$). Thus "30 per cent. Nordhausen acid" means a mixture of 30 parts by weight of SO_3 with 70 parts of H_2SO_4 . The price of SO_3 is relatively higher in weak than in strong acids, as in manufacturing it the 5 or more per cent. of water contained in ordinary "rectified oil of vitriol" must be saturated with SO_3 , each part of water requiring 4.444 parts of SO_3 to form H_2SO_4 . It is therefore decidedly more advantageous to dilute strong Nordhausen acid with the strongest obtainable rectified O.V., or still better with monohydrated sulphuric acid.

Cl. Winkler gives the following table of the specific gravities of fuming sulphuric acid at 20°C .; but it should be remarked that he worked only with "commercial acid," and that consequently all the densities found are sensibly higher than those belonging to pure acids; nor is it a matter of surprise that the values found by

Messel with another description of "commercial acid" (see below) do not entirely agree with Winkler's table.

Specific gravity at 20° C.	Percentage of		Percentage of		Percentage of	
	SO ₃ .	H ₂ O.	SO ₃ .	acid of 66° B.	free SO ₃ .	H ₂ SO ₄ .
1·860	81·84	18·16	26·45	73·55	1·54	98·46
1·865	82·12	17·88	27·57	72·43	2·66	97·34
1·870	82·41	17·59	28·76	71·24	4·28	95·76
1·875	82·63	17·37	29·95	70·05	5·44	94·56
1·880	82·81	17·19	30·38	69·62	6·42	93·58
1·885	82·97	17·03	31·03	68·97	7·29	92·71
1·890	83·13	16·87	31·67	68·33	8·16	91·84
1·895	83·43	16·66	32·52	67·48	9·34	90·66
1·900	83·48	16·52	33·09	66·91	10·07	89·93
1·905	83·57	16·43	33·46	66·54	10·56	89·44
1·910	83·73	16·27	34·10	65·91	11·43	88·57
1·915	84·08	15·92	35·52	64·48	13·33	86·67
1·920	84·56	15·44	37·27	62·73	15·95	84·05
1·925	85·06	14·94	39·49	60·51	18·67	81·33
1·930	85·57	14·43	41·56	58·44	21·34	78·66
1·935	86·23	13·77	44·23	55·77	25·65	74·35
1·940	86·78	13·22	46·46	53·54	28·03	71·97
1·945	87·13	12·87	47·88	52·12	29·94	70·06
1·950	87·41	12·59	49·01	50·99	31·46	68·54
1·955	87·65	12·35	49·98	50·02	32·77	67·23
1·960	88·22	11·78	52·29	47·71	35·87	64·13
1·965	88·93	11·08	55·13	44·87	39·68	60·32
1·970	89·83	10·17	58·81	41·19	44·64	55·36

Messel (J. Soc. Chem. Ind. 1885, p. 573) gives the following specific gravities of commercial Nordhausen acids, both at 26°·6 C., as determined by himself, and calculated for 15°·5 C. :—

Specimens.	Percentage of SO ₃ .	Specific gravities	
		at 80° F. (=26°·6 C.)	calculated for 60° F. (=15°·5 C.)
Liquid	8·3	1·842	1·852
"	30·0	1·930	1·940
Crystalline mass, resembling nitre ...	40·0	1·956	1·970
" " "	44·5	1·961	1·975
" " "	46·2	1·963	1·977
" " "	59·4	1·980	1·994
Liquid	60·8	1·992	2·006
"	65·0	1·992	2·006
"	69·4	2·002	2·016
Crystallized	72·8	1·984	1·988
"	80·0	1·959	1·973
"	82·0	1·953	1·967

CHAPTER XVI.

OTHER PROCESSES FOR MANUFACTURING
SULPHURIC ACID.

ALL the other processes which have been proposed for producing sulphuric acid, numerous as they are, can be dismissed with a very few words, since not one of them has had any technical success or promises to become successful in future. The details can be found in the places quoted.

I. *Oxidation of Sulphurous Acid by means of Nitrous Acid, but without Lead Chambers.*

Proposals for replacing the lead chambers by chambers made of india-rubber, gutta percha, slate, "zeiodelite," glass, &c. have been mentioned on p. 335.

MacDougal and Rawson (patent of Nov. 21st, 1848) conduct sulphurous acid and air through nitric acid contained in a Woulfe's bottle, in which sulphuric acid and nitrogen peroxide are generated; the latter, with the air in excess, passes through several vessels filled with water, in which the nitric acid is regenerated.

Hunt (patent of Aug. 16th, 1853) conveys a mixture of sulphurous acid and air through a tower filled with pebbles, in which nitrous vitriol continuously trickles down. This principle had already been proposed by Gay-Lussac; and it is actually carried out in the Glover towers, so far as it is practicable—that is, by conducting the escaping gases into lead chambers.

Persoz ('Technologiste,' xvii. p. 461; 'Dingler's Journal,' cxxxix. p. 427; Wagner's 'Jahresbericht,' 1856, p. 54) passes sulphurous acid through nitric acid diluted with from 4 to 6 volumes of water, and heated to 100° C., or through a mixture of nitric

acid or a nitrate with hydrochloric acid, in a comparatively small glass or stoneware vessel, promoting contact by an agitator. The gases generated by the reduction of the nitric acid ascend in condensing-towers, where they are regenerated into nitric acid by an ascending current of air and a descending jet of water. The sulphurous acid might even be diluted with carbonic acid, nitrogen, or other gases. In theory this process is right enough; in practice it is said to have failed principally from the difficulty of constructing vessels suitable for resisting the acids (?).

Verstraet's tubular apparatus ('Bulletin de la Société d'Encouragement,' 1865, p. 531; 'Dingler's Journal,' clxxix. p. 63; Wagner's 'Jahresbericht,' 1865, p. 226) has been mentioned previously (p. 377). The Jury Report of 1851 asserted that similar stoneware vessels, constructed by Fouché-Lepelletier, were at work at Javel, near Paris, and that in that factory one third of the annual make of 3600 tons was produced in them, with one third of the cubic contents and at one eighth of the cost of lead chambers. This assertion has been proved to be entirely erroneous by original correspondence in Hofmann's 'Report by the Juries,' 1862, p. 8.

Lardani's apparatus (Bull. Soc. Chim. viii. p. 295; Chem. News, 1868, No. 441, p. 238) has also been described above (p. 377); it exemplifies no essentially novel principle.

Kuhlmann (English patent, Dec. 11, 1850) proposed to force a mixture of sulphuretted hydrogen (from soda-waste) and air through nitric acid, by which nearly all the sulphur was said to be oxidized to sulphuric acid; this is, however, not the case.

Petrie (English patent, Aug. 11, 1860) employs a system of stoneware pipes filled with pebbles, through which a current of nitric acid passes from one side, and one of SO_2 and air from the other, the quantities of the materials and the construction of the apparatus being arranged in such a manner as to avoid any loss of nitric acid.

Finch and W. J. & S. Willoughby (E. P. 3086, 1884) pump a mixture of burner-gases, nitrous fumes, and steam into a tower, where they are subjected to a certain amount of pressure, in order to facilitate their combination. The escaping gases pass forward into other similar towers, and at last through a Gay-Lussac column.

W. Burns (E. P. 14441, 1886) seeks also to promote the combination of the gases by pressure, together with a peculiar kind of

agitation, in an ingeniously devised, but hardly practicable apparatus.

Hannay (E. P. 12247, 1886) passes the sulphurous and nitrous gases through a condensing tower, where they become minutely subdivided and thoroughly mixed by passing through screens, which are kept moistened by a continual stream of water trickling on them, the process being repeated until the solution of sulphuric acid formed acquires sufficient strength, when it is drawn off and a fresh supply of water is run into the apparatus.

A. & L. Q. Brin (E. P. 12070, 1886) burn pyrites with pure oxygen and convert the mixture of SO_2 and O into sulphuric acid by means of nitrous fumes. A special apparatus for this purpose is contained in my own patent of 1888, which, however, was only taken to cover the ground, the principal object of my invention being the production of sulphuric anhydride, for which the cost of pure oxygen might be more easily afforded than for ordinary sulphuric acid. That oxygen cannot be prepared, as some imagine, in a cheap way by electrolysis, employing the hydrogen evolved as fuel for dynamo-machines, has been demonstrated by Scheurer-Kestner, in criticising a proposal of Justinus Mullerus for manufacturing sulphuric acid without chambers by means of oxygen obtained in the above manner (Bull. Soc. Ind. Mulh. 1890, p. 276). 1 kilog. of oxygen (100 litres at 0° and 760 millim.) per hour would require a dynamo of $12\frac{1}{2}$ horse-power, or 131,250 calories, which means burning about $18\frac{1}{4}$ kilog. of coal, which in France cost about $3\frac{1}{2}d.$; the corresponding amount of hydrogen by its combustion would only furnish 4312 calories, or 3 per cent. of the above. A ton of real H_2SO_4 requires 490 kilog. oxygen, which would cost £7 3s.!

Durand, Hugnenin, & Co. (F. P. 205,589, May 9, 1890) pass a mixture of sulphur dioxide and air through tanks, charged with nitric acid or solutions of nitrous products, alternating with condensing-towers. The liquids are made to flow systematically through the apparatus in such manner that at last concentrated sulphuric acid, free from nitric or nitrous acid, is obtained. The above-mentioned gaseous mixture is produced by passing compressed air into sulphur- or pyrites-burners, thus also obtaining the pressure necessary for forcing the gas through the liquids contained in the tanks.

II. *Processes dispensing with Nitre.*

Gossage (Patent of Oct. 6th, 1857) burns sulphuretted hydrogen from soda-waste, cools the products of combustion, allows them to ascend in a coke-tower fed with water, runs the solution of sulphurous acid thus obtained down another coke-tower supplied with hot air, by which the SO_2 is partly changed into SO_4H_2 , and conveys the remaining SO_2 into a lead chamber, where it is completely oxidized in the usual way. According to Gossage's own avowal (Hofmann, Report, p. 9) this process is not practicable.

Petrie (Patent of Nov. 1st, 1852) allows a mixture of sulphurous acid and water, heated to 300° , to meet a spray of water in pipes of earthenware or iron filled with silica, or finely divided platinum, &c.

The observations of Doebereiner, Phillips and Magnus, Blondeau, &c. on the formation of sulphuric acid by "catalytic action" have been mentioned already on p. 850—and also those of Woehler and Mahla (Ann. Chem. Pharm. lxxi. p. 255), according to which a mixture of SO_2 and O is converted into sulphuric acid (anhydride) not only by platinum, but also by the oxides of copper, iron, or chromium at a low red heat. They expressed a hope that this reaction would become practical. A large number of attempts have been made in this direction, some of which have been mentioned in the last Chapter. To this category the above-mentioned proposals of Gossage and Petrie are in part to be referred, and those of Schmiersahl and Bouck (patented Jan. 24, 1855) and of Schneider (see preceding Chapter). All the proposals of this kind have remained equally sterile with the other new processes enumerated in the present Chapter, so far as they aimed at supplanting the lead-chamber process by a new one. This must not be confounded with Winkler's successful utilization of "catalytic action" for making anhydride, as he always starts from sulphuric acid made in the ordinary way by the chamber-process.

Hähner (Patent of March 28, 1854) employs chlorine in the presence of aqueous vapour for oxidizing SO_2 . The same process has been patented by Macfarlane (Jan. 14, 1863).

Houzé proposes (Monit. Industr. vii. p. 65) to bring sulphurous acid, air, and steam into contact in stoneware vessels at a temperature a little below a red heat. Similar vessels are said to permit distilling the acid by means of heated air or superheated steam without any bumping.

Deacon showed in 1871 (Chem. Trade J. 1889, vol. v. p. 193) that a mixture of SO_2 and atmospheric air in the presence of a solution of cupric sulphate is converted into sulphuric acid, but this seems to have become very little known. Later on the same invention was made by Roessler, and was specially applied to the absorption of acid smoke; it has been described in Chap. IV. p. 285. It is hardly applicable to the manufacture of sulphuric acid proper, but very well to that of copper sulphate from waste sulphur dioxide. The same process, extended also to salts of manganese, iron, or tin, has been patented by Clark (for Daguin), No. 3669, 1888.

III. *Sulphuric Acid from Sulphates.*

The neutral sulphates of the alkalis, the alkaline earths, and lead are as good as unchangeable at a red heat. The acid (primary) sulphates of the alkalis are first changed into pyrosulphates ($2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$); and the latter afterwards split up into neutral sulphates and sulphuric anhydride. This reaction, for obvious reasons, cannot be employed for the manufacture of sulphuric acid proper, but only for that of fuming acid, under which head it has been spoken of.

Most of the other sulphates are no better adapted for the manufacture of sulphuric acid. Only those whose metallic radicals are but very slightly positive, more particularly those which, according to the assumptions of modern chemistry, represent a sexivalent group formed by an internal linking together of two quadrivalent atoms (that is, especially ferric oxide and, though less so, alumina), and the *acid* sulphates of other radicals, yield up their sulphuric acid at a comparatively low temperature, and consequently all or the greater part of it undecomposed; the other sulphates split up at a much higher temperature, mostly decomposing into metallic oxides, sulphurous acid, and oxygen, yielding only a small portion of their sulphuric acid as such or as anhydride. Even if it were otherwise, their high price would make their employment for the manufacture of sulphuric acid impossible; most of them are themselves produced by means of ready-made sulphuric acid. From even the cheapest and most easily decomposable of all the sulphates in question, ferric sulphate, only fuming oil of vitriol can be made, and that only under especially favourable circumstances, as shown above.

There only remain the sulphates occurring in some abundance in nature as such, viz. those of baryta, lime, and magnesia. The first of these has hardly ever been seriously taken up for this purpose; but the sulphates of lime (gypsum) and of magnesia (kieserite) have very frequently been so.

Sulphuric Acid from Gypsum.

The enormous quantities of sulphuric acid occurring in nature in the shape of gypsum, and nearly worthless in this form, have occasioned many proposals for their technical utilization. These, however, have never met with any success; and least of all can any prospect of it be held out now-a-days, since such abundance of cupreous pyrites has been discovered, with which, so far as can be seen, no other material can compete in cheapness.

(1) *Production of sulphurous acid from gypsum.*—Tilghman (English patent, Feb. 1st, 1847) passes steam over red-hot gypsum; CaO is said to remain behind, and SO₂, O, and a little SO₃ to escape. For the identical process, Polony obtained an Austrian patent in 1887 (Zeitschr. f. angew. Chem. 1888, p. 57).

Cary-Mantrand (Barreswil and Girard, Dictionn. de Chim. industr. i. p. 37) exposes ignited gypsum to a current of dry HCl (whence does he get this?). CaCl₂ is formed; and SO₂, O, and SO₃ escape.

O. Siemens (Dingl. Journ. clxix. p. 207; Wagner's Jahresb. 1863, p. 208) decomposes a fused mixture of gypsum and common salt by steam. There remains behind basic calcium sulphide with a little Na₂S, Na₂SO₃, and Na₂S₂O₃; the gases given off are SO₂, HCl, and H₂S; the latter is removed by conducting CO₂ and steam at the same time into the melted mass (?). This process is the subject of strongly adverse criticism by Buff (Wagner's Jahresb. 1864, p. 170), who shows that the decomposition observed has been produced merely by the red-hot iron which forms the material of the apparatus.

Kuenzi (Wagner's Jahresb. 1858, p. 95) fluxes gypsum with quartz, sand, clay, &c. to an easily fusible slag, whilst SO₂ and O escape. The same proposal was made by Frémy, and also by Archereau (ibid. 1865, p. 271), the latter for the purpose of utilizing the oxygen as well.

O. Schott (Dingl. Journ. ccxxi. p. 442) ignites sodium sulphate, gypsum, and coal, in order to obtain a frit for glass-making; the

SO_2 is to be conveyed into a lead chamber along with the other gas and converted into sulphuric acid.

Martin (Bull. Soc. Chim. xxi. p. 47) prescribes making an artificial sulphide by smelting 1700 parts of gypsum, 1000 of ferric oxide, and 500 of coal in a blast-furnace; this is to be burnt like natural sulphides. In this case *at most* a monosulphide of iron will be obtained; and that will cost more than the best pyrites.

Scheurer-Kestner asserts that calcium or magnesium sulphate, when calcined with ferric oxide, preferably together with fluor-spar, gives off sulphuric anhydride (comp. above, p. 860).

Cummings (Amer. P. 342,785; E. P. by Lake, No. 7355, 1886) calcines a mixture of gypsum and clay in a suitable kiln; a hydraulic cement is formed, whilst SO_3 , SO_2 , and O are expelled, and are converted into sulphuric acid in the usual manner. [This is utterly hopeless with such dilute gases.]

(2) *Sulphuretted hydrogen from gypsum*.—Cary-Mantrand (*l. c.*) decomposes a mixture of gypsum and coal at a red-heat by HCl gas, whereby CaCl_2 , CO, H_2S , and S are formed.

Köhsel (Wagner's Jahresb. 1856, p. 57) decomposes gypsum reduced by coal (that is, CaS) by carbonic acid, burns the H_2S given off to SO_3 , and conveys the latter into lead chambers.

The same proposal has been made several times later, in connection with special proposals for utilizing the H_2S , of which only that of Chance (*suprà*, pp. 73 & 277) has been found to be practicable. At the present prices of pyrites even the Chance process does not seem to be economical in its application to gypsum.

(3) *Sulphuric acid direct from gypsum*.—Von Seckendorff (Wagner's Jahresb. 1855, p. 54) decomposes gypsum by lead chloride at 75°C . into CaCl_2 and PbSO_4 . A mixture of the latter salt (5 molecules) with hydrochloric acid of 33°Tw . (4 molecules) at 75°C . almost entirely decomposes into PbCl_2 (which is used for a new operation) and sulphuric acid (which is decanted and concentrated, the distilling HCl being condensed).

Shanks has patented Seckendorff's process for England (Oct. 9th, 1854).

Margueritte (patent of Dec. 22, 1854) decomposes lead phosphate by muriatic acid; hereby PbCl_2 and phosphoric acid are formed; the latter, ignited with gypsum, yields calcium phosphate and sulphuric anhydride. The calcium phosphate and lead chlo-

ride, boiled together, regenerate lead phosphate, along with CaCl_2 , which is worthless; so that the muriatic acid is always lost.

Bandiner (Wagner's *Jahresb.* 1858, p. 102), Fleck (Fabr. von chem. Prod. aus thier. Abfällen, p. 131), Reinsch (Wagner's *Jahresb.* 1870, p. 167), and other authors mention the utilization of the sulphuric acid of gypsum by treatment with a solution of ammonium carbonate, whereby ammonium sulphate is formed. This process has been used in France for some time, but it acts only incompletely.

IV. *Calcining Pyrites with Salt.*

Kenyon and Swindells (English patent, May 21st, 1872) calcine the chlorides of sodium or potassium with iron- or copper-pyrites, and treat the gas with nitric or chromic (I) acid in high towers, in order to convert the sulphurous into sulphuric acid; at the same time chlorine is given off. Wagner (*Jahresb.* 1874, p. 272) points out that in this process the sulphuric acid must remain behind in the shape of alkaline sulphates.

V. *By Electricity.*

Reynoso, in 1875, obtained a patent for causing electric sparks to pass through a compressed and cooled mixture of sulphurous acid and atmospheric air. The formation of SO_3 from a mixture of 2 vols. SO_2 and 1 vol. O by the electric spark was first observed in 1860 by H. Buff and A. W. Hofmann (*Ann. Chem. Pharm.* cxiii. p. 129); Deville (*Bull. Soc. Chem.* [2] iii. p. 366) has observed that in the presence of strong vitriol, which absorbs the SO_3 , the whole gaseous mixture can be united to form SO_3 , in this way.

CHAPTER XVII.

APPLICATIONS OF SULPHURIC ACID, AND STATISTICS.

THE *principal applications* of sulphuric acid are the following :—

I. In a more or less *dilute* state (say from 144° Tw. downwards). Above all, for making sulphate of soda (saltcake) and hydrochloric acid, and therefore ultimately for soda-ash, bleaching-powder, soap, glass, and innumerable other products. Further, for superphosphates and other artificial manures. (According to an estimate, made by Dr. R. A. Smith, in 1876, there were made in England 160,000 tons of sulphur for alkali and 100,000 tons for manures, both in the shape of pyrites.) These two applications probably consume nine tenths of all the sulphuric acid produced. Further applications are :—for preparing sulphurous, nitric, phosphoric, hydrofluoric, boric, carbonic, chromic, oxalic, tartaric, citric, acetic, and stearic acids; in preparing phosphorus, iodine, bromine, the sulphates of potassium, ammonium, barium (*blanc fixe*), calcium (*pearl hardening*); especially also for precipitating baryta or lime as sulphates for chemical processes; sulphates of magnesium, aluminium, iron, zinc, copper, mercury (as intermediate stage for calomel and corrosive sublimate); in the metallurgy of copper, cobalt, nickel, platinum, silver; for cleaning (pickling) sheet iron to be tinned or galvanized; for cleaning copper, silver, &c.; for manufacturing potassium bichromate; for working galvanic cells, such as are used in telegraphy, in electro-plating, &c.; for manufacturing ordinary ether and the composite ethers; for manufacturing garancine; for making or purifying many organic colouring-matters, especially in the oxidizing mixture of potassium bichromate and sulphuric acid; for parchment paper; for purifying many mineral oils, and sometimes coal-gas; for manufacturing starch, sirup, and sugar; for the saccharification of corn; for neutralizing the alkaline reaction of fermenting liquors, such as molasses; for effervescent drinks; for preparing tallow previously to melting it; for recovering the fatty acids from soap-suds; for destroying vege-

table fibres in mixed fabrics ; generally, in dyeing, calico-printing, tanning, as a chemical reagent in innumerable cases ; in medicine, against lead poisoning, and in many other cases.

II. *In a concentrated state.* For manufacturing the fatty acids by distillation ; purifying colza oil ; for purifying benzene, petroleum, paraffine oil, and other mineral oils ; for drying air, especially for laboratory purposes, but also for drying chlorine in Deacon's process (for this, weaker acid also, of 140° Tw., can be used) ; for the production of ice by the rapid evaporation of water in a vacuum ; for refining gold and silver, desilvering copper, &c. ; for making organo-sulphonic acids ; dissolving indigo ; preparing many nitro-compounds and nitric ethers, especially in manufacturing nitro-glycerin, pyroxyline, nitro-benzene, picric acid, and so forth.

III. *As Nordhausen fuming oil of vitriol (anhydride).* For manufacturing certain organo-sulphonic acids (in the manufacture of alizarine, eosine, &c.) ; for purifying ozokerite ; for making shoe-blackening ; for bringing ordinary concentrated acid up to the highest strength as required in the manufacture of pyroxyline and other purposes.

I have calculated the production and consumption of sulphuric acid in the United Kingdom, mostly from official sources (Chem. Ind. 1884, p. 213), on the following basis :—From the amount of pyrites imported follows the total quantity of acid made on the basis of $180 \text{ H}_2\text{SO}_4$ for each 100 pyrites. The quantity of salt decomposed, taking 7 salt = 4 pyrites, or 100 salt = $75 \text{ H}_2\text{SO}_4$, gives the quantity of acid decomposed for this purpose. The remainder will have been used mostly for manure-making, taking the acid used for other purposes as being derived mostly from brimstone. All acid is calculated as monohydrate.

Year.	Acid made from pyrites.	Used for decomposing salt.	Pyrites acid used otherwise.	Brimstone acid made.	Total acid made.
	tons.	tons.	tons.	tons.	tons.
1878	747,900	417,406	330,494	124,271	872,171
1879	716,625	445,265	271,360	126,884	833,509
1880	771,771	501,612	270,159	133,653	905,427
1881	736,797	475,724	261,073	115,599	852,396
1882	806,793	472,151	334,642	134,742	941,535
1883	815,574	484,252	331,322	125,064	940,638

These statistics are probably wrong in an important part, viz. the amount of brimstone acid made. Owing to the total want of information on the quantity of brimstone burnt for acid-making, I assumed all the brimstone imported into England to be used for this purpose, leaving the sulphur recovered from alkali waste and otherwise produced in England for the remaining uses (lucifer matches, gunpowder, &c.). But this is probably allowing far too much, for in the 25th Alkali Report (for the year 1883), where for the first time the quantity of brimstone burnt for sulphuric acid is mentioned, it is stated = 17,925 tons, which would yield about 51,300 tons of H_2SO_4 . Hence the quantity of brimstone acid in the foregoing table should be reduced by about 70,000 tons per annum, and that of the total acid made by the same figure.

The number of Sulphuric-acid works under Government inspection in England and Ireland* in the year 1889 amounted to 221, including those in which the acid was entirely used up at the works themselves for alkali, manure-making, &c. In Scotland this number was 32.

The official statistics gave the following for the production of sulphuric acid in *Germany* :—

In the year 1879	185,106 tons.
„ 1882	286,953 „
„ 1885	343,294 „
„ 1886	325,722 „
„ 1887	347,529 „
„ 1888	399,938 „

These figures are unfortunately of very little value; up to 1881 they comprise only the acid made in metallurgical establishments, after that the total acid, including that used up at the works for alkali-making, superphosphates, &c. Up to 1886 “*Englische Schwefelsäure*,” calculated as acid of 140° Tw., and Nordhausen O.V. were enumerated separately; from 1887 the figures do not distinguish between acid of 106° , 140° , 168° , and Nordhausen acid!

The quantity of acid imported into Germany in 1888 was 6711 tons, that exported 15,211 tons.

The production of sulphuric acid in Germany has been pretty accurately estimated by Hasenclever (Chem. Ind. 1884, p. 78) for the year 1882 as follows :—

Ore used.		Sulphuric acid of 142° Tw. made. tons.	Equal to H ₂ SO ₄ . tons.
	tons.		
German pyrites.....	130,892	183,249	142,934
Spanish pyrites.....	55,000	90,750	70,785
Hungarian, Norwegian, &c. pyrites.....	9,000	13,950	10,881
Mixed ores at Oker, Freiberg, Mansfeld	40,200	31,356
Zinc blende	30,000	23,400
		<hr/> 358,149	<hr/> 279,356

There were in 1888 in Germany 66 works in which sulphuric acid was a principal product, and 13 in which it was a by-product.

Italy in 1879 possessed 13 sulphuric-acid works, most of them of small size, producing 7140 tons of acid of 106°, 2210 tons of 172°, and 2520 tons of 168° Tw.; say altogether, 9883 tons H₂SO₄. Since that time the production of sulphuric acid has probably more than doubled.

The production of sulphuric acid in *France* amounted in 1867 to 90,000 tons, in 1877 to 150,000 tons, in 1889 to about 234,000 tons. The quantity of sulphuric acid exported in 1889 was 13,190 tons, that imported 6758 tons.

In *Austria* the exportation and importation of sulphuric acid nearly balances itself, the amounts of each being about 4000 or 5000 tons per annum. (Particulars in 'Chem. Ind.' 1889, p. 474.)

In the *United States* (according to information from Dr. Weidig) there existed, in 1891, 114 sulphuric-works, producing about 500,000 tons O.V. per annum.

APPENDIX.

To p. 20. *Occurrence of Brimstone in America.*—A very large deposit of sulphur has been recently discovered in the Grand Gulf Basin, near Lake Charles City, in the parish of Calcasieu, State of Louisiana. Two wells have been bored at different localities, which struck sulphur at a depth of about 450 feet. The first and thickest bed of sulphur is from 108 to 112 feet thick ; it contains near the top 62 per cent., in the centre 90 per cent. of pure sulphur. One of the wells has been continued lower down, and proved the existence of several smaller beds of rich brimstone-ore, and several hundred feet of gypsum containing sulphur ; in the other well no gypsum, but calcareous substance containing sulphur is found. The working presents a difficulty in the presence of several hundred feet of quicksand on the top of the brimstone beds ; but it is expected that this will be overcome in the course of 1892, when the above mine (the property of the American Sulphur Company, of New York) may become one of the most important in the world.

During the years 1888, 1889, and 1890 no brimstone was produced in the United States, the Cove Creek works having stopped early in 1888.

To p. 34. *Production of Iron Pyrites in the United Kingdom :* in 1888, 23,507 tons ; in 1889, 17,719 tons ; in 1890, 16,018 tons.

To p. 48. *Pyrites in the United States.*—Output of all the mines in 1888, 54,331 tons ; in 1889 much more ; in 1890, 97,706 tons.

Imports of pyrites into the United States :—

Year.	Long tons.	Year.	Long tons.
1881	11,927	1886	60,000
1882	29,818	1887	60,000
1883	35,811	1888	81,000
1884	44,250	1889	100,000
1885	50,000	1890	115,000

(Eng. & Min. Journal, 1891, p. 45.)

To p. 73. *Employment of sulphuretted hydrogen for the manufacture of sulphuric acid.*—An anonymous inventor has proposed to absorb this gas in hydrated ferric oxide suspended in water, filter, press the residue, dry it, and burn it on shelf-burners. Wyss (Bull. Soc. ind. Mulh. 1890, p. 281) has shown that this process is neither novel nor in any way promising of success.

To p. 83. *Specific gravity of nitric acid.*—For the table given in the text, the more accurate table from the results of Lunge and Rey (Zeitsch. f. angew. Chem. 1891, p. 165) should be substituted. The specific gravities are taken at 15° C., referred to water of 4° and reduced to the vacuum. They refer to *chemically pure* nitric acid; commercial acid, containing nitrous acid, &c., contains less real HNO_3 at the same specific gravity.

Specific gravities 15° at 4°.	Degrees Twadd.	100 parts by weight contain		1 litre contains kilog.	
		N_2O_5 .	HNO_3 .	N_2O_5 .	HNO_3 .
1·000	0	0·08	0·10	0·001	0·001
1·005	1	0·85	1·00	0·008	0·010
1·010	2	1·62	1·90	0·016	0·019
1·015	3	2·39	2·80	0·024	0·028
1·020	4	3·17	3·70	0·033	0·038
1·025	5	3·94	4·60	0·040	0·047
1·030	6	4·71	5·50	0·049	0·057
1·035	7	5·47	6·38	0·057	0·066
1·040	8	6·22	7·26	0·064	0·075
1·045	9	6·97	8·13	0·073	0·085
1·050	10	7·71	8·99	0·081	0·094
1·055	11	8·43	9·84	0·089	0·104
1·060	12	9·15	10·68	0·097	0·113
1·065	13	9·87	11·51	0·105	0·123
1·070	14	10·57	12·33	0·113	0·132
1·075	15	11·27	13·15	0·121	0·141
1·080	16	11·96	13·95	0·129	0·151
1·085	17	12·64	14·74	0·137	0·160
1·090	18	13·31	15·53	0·145	0·169
1·095	19	13·99	16·32	0·153	0·179

TABLE (continued).

Specific gravities 15° at 4°.	Degrees Twadd.	100 parts by weight contain		1 litre contains kilog.	
		N ₂ O ₅ .	HNO ₃ .	N ₂ O ₅ .	HNO ₃ .
1·100	20	14·67	17·11	0·161	0·188
1·105	21	15·34	17·89	0·170	0·198
1·110	22	16·00	18·67	0·177	0·207
1·115	23	16·67	19·45	0·186	0·217
1·120	24	17·34	20·23	0·195	0·227
1·125	25	18·00	21·00	0·202	0·236
1·130	26	18·66	21·77	0·211	0·246
1·135	27	19·32	22·54	0·219	0·256
1·140	28	19·98	23·31	0·228	0·266
1·145	29	20·64	24·08	0·237	0·276
1·150	30	21·29	24·84	0·245	0·286
1·155	31	21·94	25·60	0·254	0·296
1·160	32	22·60	26·36	0·262	0·306
1·165	33	23·25	27·12	0·271	0·316
1·170	34	23·90	27·88	0·279	0·326
1·175	35	24·54	28·63	0·288	0·336
1·180	36	25·18	29·38	0·297	0·347
1·185	37	25·83	30·13	0·306	0·357
1·190	38	26·47	30·88	0·315	0·367
1·195	39	27·10	31·62	0·324	0·378
1·200	40	27·74	32·36	0·333	0·388
1·205	41	28·36	33·09	0·342	0·399
1·210	42	28·99	33·82	0·351	0·409
1·215	43	29·61	34·55	0·360	0·420
1·220	44	30·24	35·28	0·369	0·430
1·225	45	30·88	36·03	0·378	0·441
1·230	46	31·53	36·78	0·387	0·452
1·235	47	32·17	37·53	0·397	0·463
1·240	48	32·82	38·29	0·407	0·475
1·245	49	33·47	39·05	0·417	0·486
1·250	50	34·13	39·82	0·427	0·498
1·255	51	34·78	40·58	0·437	0·509
1·260	52	35·44	41·34	0·447	0·521
1·265	53	36·09	42·10	0·457	0·533
1·270	54	36·75	42·87	0·467	0·544
1·275	55	37·41	43·64	0·477	0·556
1·280	56	38·07	44·41	0·487	0·568
1·285	57	38·73	45·18	0·498	0·581
1·290	58	39·39	45·95	0·508	0·593
1·295	59	40·05	46·72	0·519	0·605
1·300	60	40·71	47·49	0·529	0·617
1·305	61	41·37	48·26	0·540	0·630
1·310	62	42·06	49·07	0·551	0·643
1·315	63	42·76	49·89	0·562	0·656
1·320	64	43·47	50·71	0·573	0·669
1·325	65	44·17	51·53	0·585	0·683
1·330	66	44·89	52·37	0·597	0·697
1·335	67	45·62	53·22	0·609	0·710
1·340	68	46·35	54·07	0·621	0·725
1·345	69	47·08	54·93	0·633	0·739
1·350	70	47·82	55·79	0·645	0·753
1·355	71	48·57	56·66	0·658	0·768

TABLE (continued).

Specific gravities at 15° at 4°.	Degrees Twadd.	100 parts by weight contain		1 litre contains kilog.	
		N ₂ O ₅ .	HNO ₃ .	N ₂ O ₅ .	HNO ₃ .
1.360	72	49.35	57.57	0.671	0.783
1.365	73	50.13	58.48	0.684	0.798
1.370	74	50.91	59.39	0.698	0.814
1.375	75	51.69	60.30	0.711	0.822
1.380	76	52.52	61.27	0.725	0.846
1.385	77	53.35	62.24	0.739	0.862
1.390	78	54.20	63.23	0.753	0.879
1.395	79	55.07	64.25	0.768	0.896
1.400	80	55.97	65.30	0.783	0.914
1.405	81	56.92	66.40	0.800	0.933
1.410	82	57.86	67.50	0.816	0.952
1.415	83	58.83	68.63	0.832	0.971
1.420	84	59.83	69.80	0.849	0.991
1.425	85	60.84	70.98	0.867	1.011
1.430	86	61.86	72.17	0.885	1.032
1.435	87	62.91	73.39	0.903	1.053
1.440	88	64.01	74.68	0.921	1.075
1.445	89	65.13	75.98	0.941	1.098
1.450	90	66.24	77.28	0.961	1.121
1.455	91	67.38	78.60	0.981	1.144
1.460	92	68.56	79.98	1.001	1.168
1.465	93	69.79	81.42	1.023	1.192
1.470	94	71.06	82.90	1.045	1.219
1.475	95	72.39	84.45	1.068	1.246
1.480	96	73.76	86.05	1.092	1.274
1.485	97	75.18	87.70	1.116	1.302
1.490	98	76.80	89.60	1.144	1.335
1.495	99	78.52	91.60	1.174	1.369
1.500	100	80.65	94.09	1.210	1.411
1.501	—	81.09	94.60	1.217	1.420
1.502	—	81.50	95.08	1.224	1.428
1.503	—	81.91	95.55	1.231	1.436
1.504	—	82.29	96.00	1.238	1.444
1.505	101	82.63	96.39	1.244	1.451
1.506	—	82.94	96.76	1.249	1.457
1.507	—	83.26	97.13	1.255	1.464
1.508	—	83.58	97.50	1.260	1.470
1.509	—	83.87	97.84	1.265	1.476
1.510	102	84.09	98.10	1.270	1.481
1.511	—	84.28	98.32	1.274	1.486
1.512	—	84.46	98.53	1.277	1.490
1.513	—	84.63	98.73	1.280	1.494
1.514	—	84.78	98.90	1.283	1.497
1.515	103	84.92	99.07	1.287	1.501
1.516	—	85.04	99.21	1.289	1.504
1.517	—	85.15	99.34	1.292	1.507
1.518	—	85.26	99.46	1.294	1.510
1.519	—	85.35	99.57	1.296	1.512
1.520	104	85.44	99.67	1.299	1.515

*Correction of the observed specific gravities for temperatures
a little above or below 15° C.*

		Add for -1° C. Deduct for +1° C.
With spec. grav. between	1·000—1·020	0·0001
”	” 1·021—1·040	0·0002
”	” 1·041—1·070	0·0003
”	” 1·071—1·100	0·0004
”	” 1·101—1·130	0·0005
”	” 1·131—1·160	0·0006
”	” 1·161—1·200	0·0007
”	” 1·201—1·245	0·0008
”	” 1·245—1·280	0·0009
”	” 1·281—1·310	0·0010
”	” 1·113—1·350	0·0011
”	” 1·351—1·365	0·0012
”	” 1·366—1·400	0·0013
”	” 1·401—1·435	0·0014
”	” 1·436—1·490	0·0015
”	” 1·491—1·500	0·0016
”	” 1·501—1·520	0·0017

To p. 92. *Guttmann's Condensing-apparatus for Nitric Acid*, consisting entirely of pipes, is shown in figs. 373 and 374. It is supplied by Ludwig Rohrmann, of Krauschwitz, near Muskau, in Silesia. The apparatus is patented in England (No. 8915, of 1890), and answers its purpose very well, especially for strong acids. Its description has been more specially given in *Zeitschr. f. angew. Chemie*, 1880, p. 507, and 1891, p. 238. The tubular form of the apparatus acts all the better in the condensation of the acid, as the thickness of the walls is only $\frac{1}{8}$ inch, in spite of their length (upwards of 8 feet). All the joints run perpendicular, or in an angle of 45°, and never show any leakage. The condensed acid runs away through the small pipes at the bottom into a common receiver; hydraulic seals prevent any gas from going the same way. The gases are ultimately passed through a Lunge-Rohrmann's plate-column (comp. *supra*, p. 91), where they are brought into intimate contact with water and air, and almost the last traces of nitrogen oxides are taken out of them. This apparatus is particularly well adapted for the manufacture of the

Fig. 378.

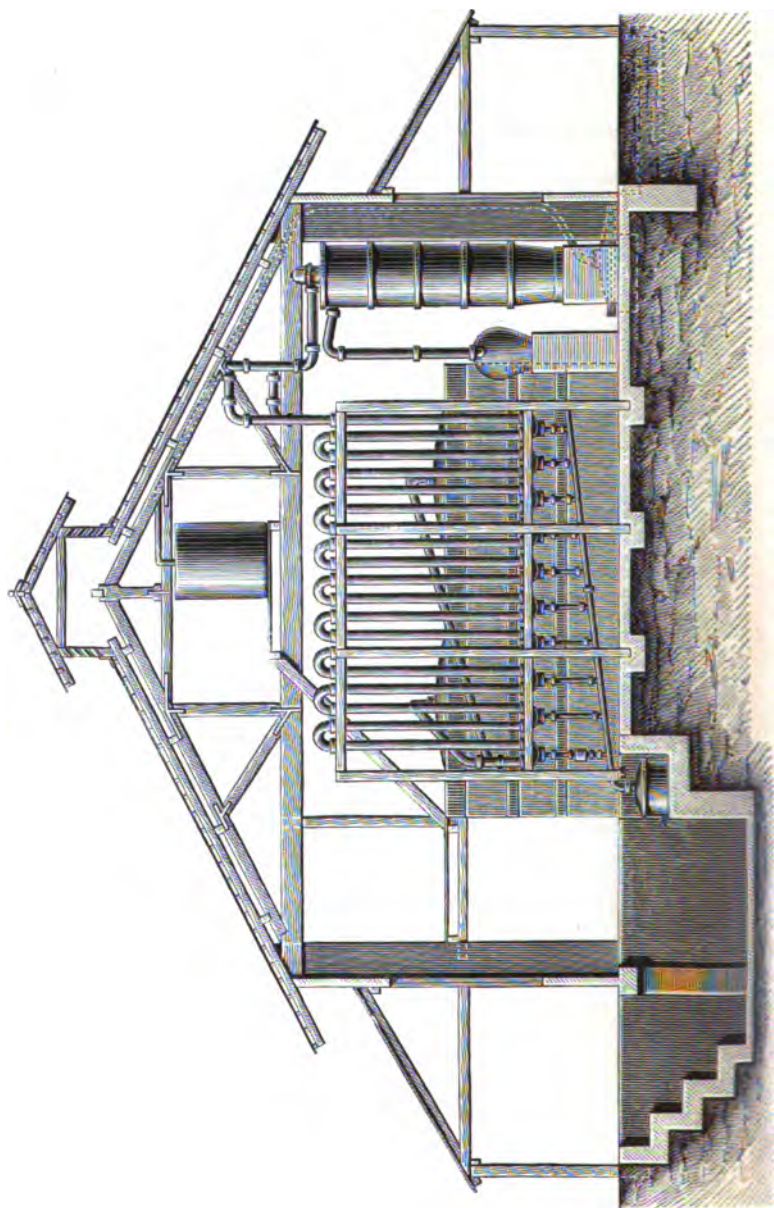
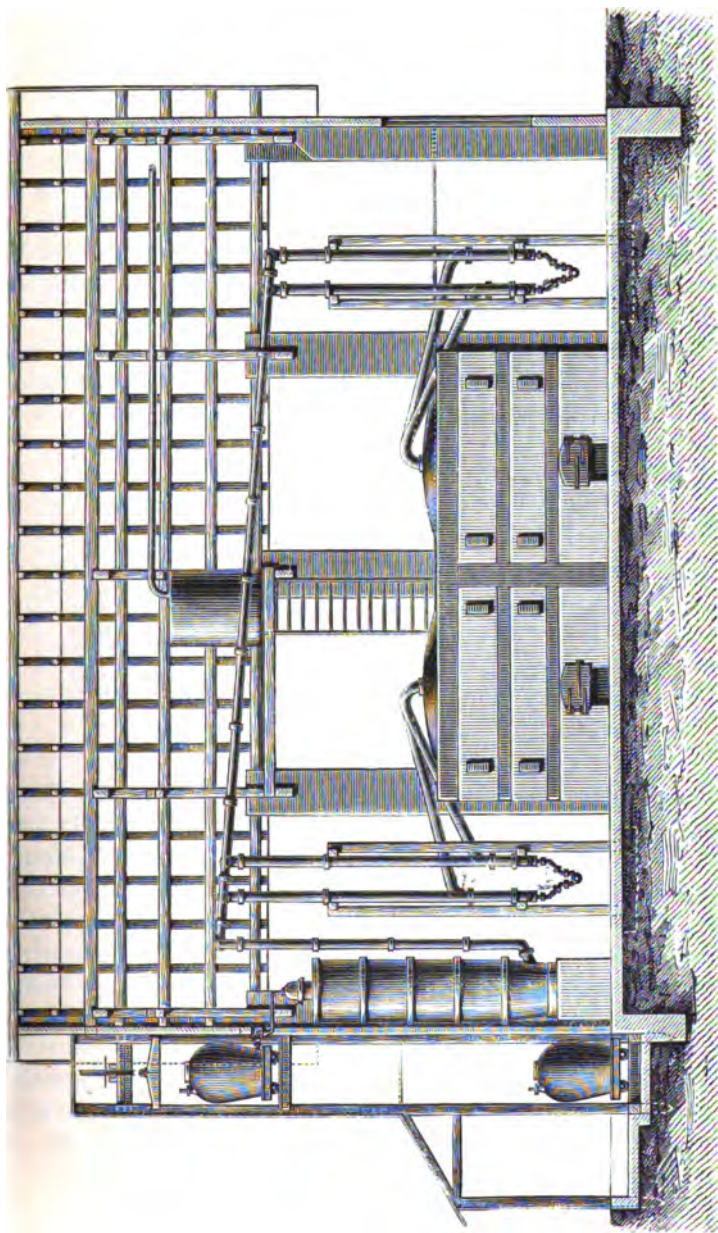


Fig. 374.



strongest acid, as required for nitroglycerin-making and similar purposes. It admits of driving the retorts much more quickly than usual, so that a charge of 12 cwt. nitre can be finished off in 10 or 11 hours. Even when running the weak acid from the plate-column to waste, the total loss averages only 7·4 per cent. of the theoretically obtainable acid; sometimes it was as low as 3 per cent. Where the weak acid from the column (which can be got up to 60° or 80° Tw.) can be used up, the loss will be almost *nil*. But even where that weak acid is run to waste, the plate-column should not be omitted, as otherwise the draught is too strong and the loss of acid, in spite of all precautions, rises to 12 per cent.

To p. 100. *Specific gravity of sulphurous-acid solutions*.—Giles and Shearer (J. Soc. Chem. Ind. 1885, p. 305) give the following table of the percentage of SO₂ in solutions of various specific gravities :—

Temp.	Spec. Grav.	Per cent. SO ₂	Temp.	Spec. Grav.	Per cent. SO ₂
15°·5 C.	1·0051	0·99	15°·5 C.	1·0399	8·08
"	1·0102	2·05	"	1·0438	8·68
"	1·0148	2·87	"	1·0492	9·80
"	1·0204	4·04	"	1·0541	10·75
"	1·0252	4·99	12°·5	1·0597	11·65
"	1·0297	5·89	11°·0	1·0668	13·09
"	1·0353	7·01			

To p. 144. *Action of sulphuric acid on lead*.—Since there are serious contradictions concerning the action of sulphuric acid on lead of different degrees of purity, I have, in conjunction with Mr. E. Schmid, undertaken a thorough examination of that subject, varying not merely the description of lead but also the presence or absence of nitrous and nitric acid, the concentration, and the temperatures. Some hundreds of experiments have been already made, but the investigation is not yet concluded, and I therefore state only a few general results.

1st. Pure, soft lead suffers in all cases less chemical attack than hard lead, containing 1·8 per cent. antimony, or the alloy of 18 parts of antimony and 82 parts of lead. With the rise of temperature the differences increase very quickly.

2nd. Sulphuric acid containing nitrous acid (nitrous vitriol) acts more strongly than pure acid at all temperatures and on all descriptions of lead.

3rd. The presence of air in all cases increases the action of nitrous vitriol.

4th. The gas evolved on contact of sulphuric acid with lead (which is nearly pure hydrogen) is no measure of the corrosion. Pure lead, whilst suffering much less loss of weight than such containing antimony, yields far more gas than the latter, whose loss of weight is two hundred times greater than could be calculated from the quantity of gas given off. This observation shows that in the special case where sulphuric acid is to be kept or sent out in closed leaden vessels the lead employed should not be pure, because the gas evolved would exert great pressure and cause the lead to bulge out.

Our observations seem to disagree with the assertion recently made by Hochstetter that lead containing as little as 0.02 per cent. copper, or a larger quantity of the same metal or of antimony, stands the action of sulphuric acid incomparably better than pure "virgin" lead. But as Hochstetter made merely practical tests on the large scale, he may have confounded mechanical with chemical resistance; or his "virgin" lead may have contained oxygen (litharge), which is believed to be very prejudicial in such cases. I propose to elucidate that question, if possible.

Schmid and I have further made a number of experiments (to be published later on) in order to determine under what circumstances the *dilution of nitrous vitriol with water* increases its action on lead—a question of much importance in connection with the working of the last vitriol chamber of a set. If nitrous vitriol is diluted with water, its nitrous acid is partially (in the end entirely) split up into nitric oxide and nitric acid, and it is the latter whose action must appear dangerous. Our preliminary results (to be supplemented by further experiments) show the following average losses of pure lead after several days' action at 50° C.:—

No.	Spec. grav. of acid.	Per cent. N_2O_3 .	Per cent. N_2O_5 .	Loss of weight per sq. centim. of lead.
1.	1.710	0.958	0.062	milligr. 1.97
2.	1.500	0.561	0.169	0.68
3.	1.395	0.322	0.254	1.15
4.	1.300	0.267	0.212	2.12
5.	1.300	1.259	1.974	7.95

Acids 2, 3, and 4 were prepared by diluting acid 1 with water; acid 5 by adding a small quantity of nitric acid to No. 4. We find that strong nitrous vitriol acts rather more than that which is moderately concentrated, say to the strength of ordinary chamber acid. When diluting to spec. grav. 1.4 the attack is already more pronounced, and at spec. grav. 1.3 it exceeds that at spec. grav. 1.71, which can be ascribed only to the nitric acid formed. When a little of the latter was purposely added, the action was almost quadrupled.

The experiments of Veley (J. Soc. Chem. Ind. 1891, p. 211), according to which mixtures of nitrous and nitric acid have a stronger action on lead than either acid by itself, have no practical bearing on the behaviour of the acid in vitriol chambers, since if nitric acid occurs there it is always accompanied by nitrous acid, and, what is far more important, the immense excess of sulphuric acid greatly modifies all conditions of the case.

To p. 158. *Tension of nitrous acid in the presence of sulphuric acid of various strengths at different temperatures.*—The figures given in the text (from Sorel's observations) have now become obsolete by the far more extended observations published by myself in the Zeitsch. f. angew. Chemie, 1891, p. 37 *et seq.* The tables constructed from these indicate the loss of N_2O_3 suffered by acids of four different concentrations, containing quantities of N_2O_5 varying from 1 gram per litre upwards, in a current of air at temperatures from 50° to 90° C.

1. Nitrous vitriol of spec. grav. 1.720 (say, 78 per cent. H_2SO_4).

N_2O_3 originally present. Grams in 1 litre.	Loss of N_2O_3 in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
1	0.006
2	0.018
3	0.025
4	0.031
5	0.037
6	0.043
7	0.056
8	0.010	0.068
9	0.012	0.081
10	0.018	0.093
11	0.025	0.112
12	0.030	0.125
13	0.031	0.143
14	0.043	0.168
15	0.006	0.056	0.193
16	0.010	0.068	0.218
17	0.006	0.087	0.250
18	0.012	0.106	0.281
19	0.025	0.125	0.318
20	0.031	0.150	0.356
21	0.043	0.175	0.400
22	0.062	0.200	0.450
23	...	0.006	0.031	0.237	0.500
24	0.006	0.018	0.100	0.275	0.550
25	0.012	0.031	0.125	0.312	0.600
26	0.018	0.043	0.150	0.356	0.662
27	0.031	0.062	0.181	0.400	0.725
28	0.043	0.081	0.212	0.450	0.800
29	0.062	0.100	0.256	0.500	0.850
30	0.081	0.125	0.293	0.550	0.956
31	0.093	0.162	0.337	0.612	1.043
32	0.112	0.200	0.387	0.641	1.125
33	0.125	0.237	0.391	0.743	1.206
34	0.143	0.275	0.475	0.806	1.287
35	0.156	0.312	0.525	0.868	1.375
36	0.175	0.350	0.575	0.931	1.456
37	0.193	0.381	0.618	1.000	1.543
38	0.206	0.418	0.662	1.062	1.625
39	0.237	0.456	0.718	1.125	1.712
40	0.268	0.500	0.775	1.193	1.800
41	0.293	0.543	0.831	1.256	1.890
42	0.325	0.587	0.887	1.331	1.975
43	0.350	0.631	0.937	1.400	2.062
44	0.376	0.675	0.993	1.468	2.150
45	0.406	0.712	1.050	1.537	2.237
46	0.437	0.756	1.106	1.606	2.325
47	0.462	0.800	1.162	1.675	2.392
48	0.493	0.837	1.218	1.743	2.500
49	0.518	0.881	1.268	1.806	2.587
50	0.550	0.931	1.325	1.875	2.675

2. Acid of spec. grav. 1.686 (say, 76 per cent. H_2SO_4).

N_2O_5 originally present. Grams in 1 litre.	Loss of N_2O_5 in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
8	0.025
9	0.036
10	0.012	0.050
11	0.018	0.062
12	0.025	0.086
13	0.010	0.050	0.125
14	0.012	0.075	0.162
15	0.025	0.100	0.225
16	0.050	0.150	0.286
17	...	0.010	0.062	0.200	0.350
18	...	0.012	0.100	0.262	0.436
19	...	0.025	0.150	0.350	0.525
20	...	0.050	0.186	0.425	0.625
21	...	0.075	0.250	0.525	0.750
22	...	0.112	0.300	0.650	0.975
23	...	0.136	0.350	0.775	1.200
24	...	0.175	0.400	0.900	1.436
25	0.010	0.200	0.462	1.025	1.662
26	0.012	0.236	0.512	1.175	1.900
27	0.025	0.262	0.562	1.300	2.125
28	0.036	0.300	0.612	1.436	2.350
29	0.050	0.336	0.675	1.575	2.600
30	0.062	0.362	0.750	1.700	2.812
31	0.100	0.412	0.850	1.812	3.086
32	0.136	0.462	0.950	1.975	3.350
33	0.186	0.512	1.050	2.100	3.625
34	0.225	0.575	1.150	2.236	3.900
35	0.275	0.625	1.250	2.362	4.175
36	0.312	0.675	1.336	2.500	4.450
37	0.350	0.725	1.436	2.625	4.736
38	0.400	0.825	1.536	2.762	5.000
39	0.436	0.836	1.636	2.900	5.275
40	0.486	0.886	1.736	3.025	5.550
41	0.550	0.950	1.850	3.150	5.850
42	0.612	1.050	1.986	3.275	6.125
43	0.686	1.125	2.112	3.412	6.400
44	0.750	1.212	2.250	3.525	6.700
45	0.825	1.300	2.325	3.736	6.975
46	0.886	1.386	2.500	3.825	7.250
47	0.962	1.475	2.636	3.962	7.536
48	1.025	1.512	2.762	4.100	7.825
49	1.100	1.650	2.886	4.236	8.100

3. Acid of spec. grav. 1.633 (say, 71.5 per cent. H_2SO_4).

N ₂ O ₃ originally present. Grams in 1 litre.	Loss of N ₂ O ₃ in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
1	0.012	0.025	0.036	0.100	0.150
2	0.050	0.075	0.086	0.225	0.300
3	0.100	0.150	0.186	0.350	0.436
4	0.162	0.212	0.300	0.536	0.612
5	0.212	0.300	0.436	0.736	0.825
6	0.300	0.425	0.636	1.000	1.112
7	0.400	0.562	0.836	1.275	1.425
8	0.500	0.712	1.036	1.550	1.750
9	0.600	0.835	1.236	1.812	2.062
10	0.700	0.936	1.436	2.086	2.375
11	0.800	1.125	1.636	2.350	2.712
12	0.871	1.262	1.825	2.636	3.075
13	0.986	1.400	2.036	2.900	3.436
14	1.086	1.536	2.225	3.175	3.800
15	1.186	1.675	2.412	3.450	4.162
16	1.275	1.800	2.612	3.725	4.512
17	1.375	1.936	2.786	4.000	4.886
18	1.475	2.036	2.975	4.262	5.236
19	1.562	2.250	3.186	4.550	5.600
20	1.662	2.412	3.400	4.850	5.986
21	1.812	2.612	3.650	5.162	6.400
22	1.975	2.812	3.912	5.512	6.862
23	2.186	3.062	4.250	5.912	7.425
24	2.436	3.336	4.612	6.350	8.036
25	2.700	3.636	5.000	6.800	8.662
26	3.000	3.950	5.412	7.300	9.362
27	3.312	4.300	5.850	7.812	10.150
28	3.662	4.636	6.325	8.400	11.000
29	4.025	5.012	6.812	9.025	11.986
30	4.412	5.412	7.350	9.675	13.125
31	4.800	5.836	7.950	10.386	14.500
32	5.236	6.325	8.575	11.175	16.362

4. Acid of spec. grav. 1·60 (say, 69 per cent. H_2SO_4).

N_2O_5 originally present. Grams in 1 litre.	Loss of N_2O_5 in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
1	0·050	0·086	0·175	0·336	0·412
2	0·100	0·236	0·436	0·725	0·912
3	0·325	0·525	0·775	1·150	1·500
4	0·562	0·836	1·250	1·910	2·100
5	0·812	1·150	1·500	2·120	2·700
6	1·050	1·450	1·900	2·500	3·350
7	1·286	1·800	2·350	3·100	4·112
8	1·512	2·150	2·800	3·725	4·900
9	1·750	2·425	3·250	4·336	5·686
10	1·975	2·812	3·712	4·900	6·475
11	2·250	3·162	4·436	5·625	7·300
12	2·512	3·536	4·675	6·325	8·125
13	2·786	3·936	5·150	7·012	8·962
14	3·065	4·250	5·650	7·700	9·750
15	3·360	4·612	6·125	8·400	10·625
16	3·600	4·975	6·612	9·125	11·462
17	3·862	5·350	7·100	9·525	12·250
18	4·150	5·712	7·600	10·462	13·136
19	4·425	6·075	8·086	11·350	13·975
20	4·700	6·425	8·562	11·850	14·800

To p. 165. *Methyl-orange as indicator* is not applicable in the presence of nitrous acid, which destroys it. In this case (*e.g.* with very impure sulphuric acid) another indicator must be chosen, say litmus, or the nitrous acid must be removed, *e.g.* by means of potassium permanganate.

To p. 257. *Working dust-burners*.—Crowder (J. Soc. Chem. Ind. 1891, p. 298), in working with shelf-burners containing seven beds, charged once every eight hours (so that the charge takes $7 \times 8 = 56$ hours to complete the course), found the following percentages of sulphur on the different shelves (nearly agreeing with Sorel's results mentioned in the text) :—

	Average of 23 trials.	Ditto of 26 trials.	
Ore charged.....	50	50	per cent. S.
No. 1 shelf	32·27	32·81	„
2 „	21·41	17·55	„
3 „	12·77	11·09	„
4 „	6·39	5·05	„
5 „	4·08	3·42	„
6 „	2·35	2·56	„
7 „	2·27	1·96	„

To p. 270. *Combination of lump-burners and dust-burners for the same set of chambers.*—Such a combination is generally avoided, as the conditions of draught are very different in both cases. I have, however, seen a combination of the above-mentioned kind in excellent work at the Stassfurt potash-works managed by Dr. Bernhardt, the good result being brought about by placing the shelf-burners so low that the top shelf is at a level with the charging-door of the lump-burners. This causes an upward draught in the shelf-burner, and prevents their blowing out, even when the doors are opened.

To p. 276. *Roasting of zinc-blende.*—In the newest shape of Hasenclever's furnace, mentioned in the text, constructed on Liebig's principle, the top muffle should be about 580° to 690° hot, the two following ones 750° to 900° . The progress of the roasting is apparent from the following percentages of sulphur:—

In green ore.....	19.2	26.8	26.5
At the end of the first muffle ...	17.6	19.1 -21.9	15.9 -21.4
„ „ second „ ...	12.0	11.2 -14.3	9.9 -12.4
„ „ third „ ...	3.4	1.02- 1.48	0.75- 1.06
After complete roasting	0.6	0.35- 1.02	—

(Fischer's Jahresh. 1890, p. 444.)

To p. 294. An improved *column for boiling solutions of sulphuric acid* has been patented by Haenisch (G. P. 52,025).

To p. 318. *Formation of sulphuric anhydride when burning sulphur.*—Hempel (Ber. d. deutsch. chem. Ges. 1890, p. 1455) found that, on burning limestone in oxygen at the ordinary atmospheric pressure, about 2 per cent. of it was converted into SO_3 (which agrees with my results, as given in the text); but when effecting the combustion under a pressure of 40 or 50 atmospheres, about half of the sulphur was converted into SO_3 .

To p. 322. *Composition and temperature of burner-gas.*—Crowder (J. Soc. Chem. Ind. 1891, p. 298) quotes the following observations of the volume-percentage of burner-gas (details in the original; no account is taken of the SO_3 present):—

	SO ₂	O.
Lump-kilns.....	from 4·97 to 6·33	9·60 to 11·21
Old dust-kilns (shelf-burners) „	6·03 „ 7·02	9·10 „ 10·00
Ditto, another ore	„ 6·34 „ 7·43	7·78 „ 8·82
New dust-kilns	„ 4·86 „ 7·03	8·98 „ 10·68

The temperature of the gas, where it enters the Glover tower, in the case of lump-burners is between the melting-points of zinc (412° C.) and antimony (432°). The gas from dust-burners, which has first to traverse a series of dust-chambers, is generally hot enough to melt lead (=326°), but it is sometimes rather less.

To p. 363. *Shape of chambers*.—E. and T. Deplace (E. P. 5058, 1890) describe an annular chamber, in which the gaseous current is continuously changing its direction, owing to that shape.

[No doubt the gases will become better mixed in this way, but this advantage will probably be more than counterbalanced by the smaller cooling-action of the inner wall, quite apart from the troublesome and expensive construction of such a chamber. The object in question can be much more simply attained by other means described in the text of this book.]

To p. 380. *Lunge's proposal for diminishing the chamber-space by placing "plate-columns" between the chambers* has found several practical applications since the text was printed. The results so far have been extremely satisfactory. In a special case, at a Bohemian works, the placing of a column of 16 layers of plates between the first and the second chamber of a set of two at once permitted charging 30 per cent. more pyrites, whilst the yield of acid remained the same, and the consumption of nitre actually went down. But as it was found that the second chamber now made no acid whatever, and might have been dispensed with entirely, except for cooling and drying the gases before entering the Gay-Lussac tower, the column in reality increased the working capacity of the first chamber by 70 per cent.

To p. 395. *Acid-drips*.—The cylinders for these are generally made much too large, so that they show the changes in the process much too slowly. It is therefore preferable on all accounts to make the cylinders very small, say holding about 20 cubic centimetres, with a side tube and funnel, into which the fresh drips fall, as shown in fig. 145, whilst the cylinder itself keeps

overflowing, and thus its contents are renewed about once in every ten minutes. Special small hydrometers, showing only a range of, say, between 20 degrees Twaddell, are made for the purpose of showing the strength of acid in these small drips.

To p. 426. *Mechanical apparatus for the production of draught in vitriol-chambers.*—A similar arrangement to that at the zinc-works mentioned in the text is found at the Halsbrücke works, near Freiberg, where the burner-gases have to pass through flues nearly a thousand feet long, in order to deposit the arsenic. The necessary draught is produced by means of Roots's blowers, made of an alloy of lead and antimony, which both aid in the roasting off of the ore and in producing good working conditions in the chambers.

To p. 458. *Strength of acid in chambers.*—Crowder (J. Soc. Chem. Ind. 1891, p. 301) prefers placing the "drips" in the connecting-pipes between the chambers, and keeps them as nearly as possible at the following strengths:—drip from Glover tower to 1st chamber = 95° to 105° ; from 1st to 2nd chamber = 130° ; from 2nd to 3rd chamber = 122° ; from 3rd to 4th chamber = 105° ; from 4th chamber to Gay-Lussac = 85° . If the drip from No. 1 to No. 2 chamber stands lower than 130° , the consumption of nitre is increased. [The drips in the connecting-pipes do not correctly indicate the work done in the chamber, as in consequence of the far greater cooling-action the formation of acid in these places must be abnormally large; comp. p. 625.]

To p. 474. *Temperature of the chambers.*—Further observations on this subject have been published by Crowder (J. Soc. Chem. Ind. 1891, p. 301), with no novel results.

To p. 486. *Composition of chamber-gases.*—Crowder (J. Soc. Chem. Ind. 1890, p. 302) quotes the results found with gases taken from testing-holes in the connecting-pipes:—

	Lump-ore kilns.		Dust-kilns.	
	SO ₂ .	O.	SO ₂ .	O.
From Glover-tower to No. 1 chamber.	6.9	8.0	5.2	11.8
" No. 1 to No. 2	4.4	7.5	2.4	11.8
" No. 2 to No. 3	1.9	5.7	1.2	10.6
" No. 3 to No. 4	0.4	0.1	0.6	10.2
" No. 4 to Gay-Lussac	0.3	5.7	0.4	9.3

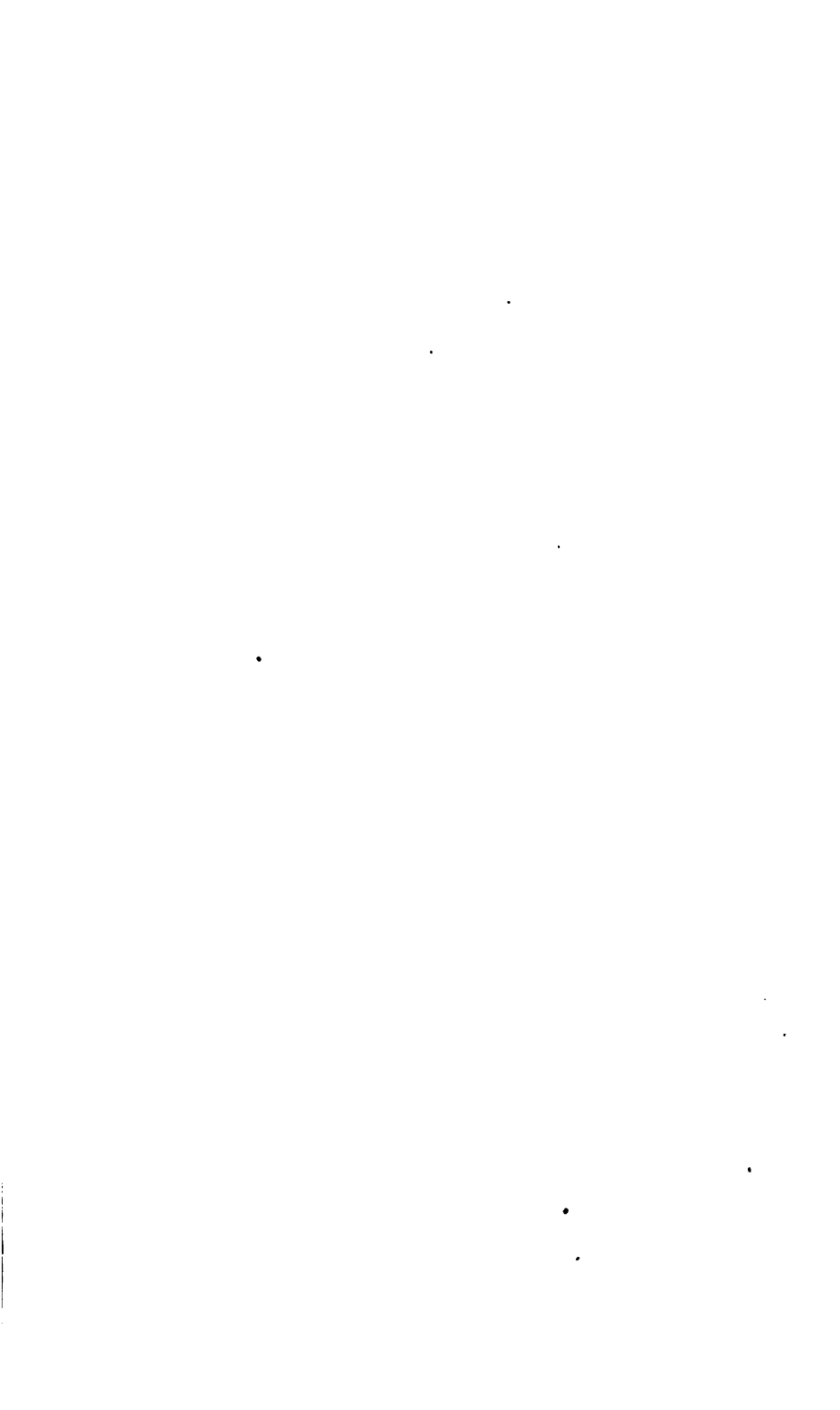
Another series from a Scotch works, with a set of 6 chambers:—

	SO ₂ .	O.
Glover-tower to No. 1	6.32	12.55
No. 1 to No. 2	4.44	11.89
No. 2 to No. 3	2.63	11.28
No. 3 to No. 4	1.40	10.86
No. 4 to No. 5	0.70	10.61
No. 5 to No. 6	0.26	10.46
No. 6 to Gay-Lussac	0.035	10.38

To p. 553. *Cooling the acid for feeding the Gay-Lussac tower.*—Crowder (J. Soc. Chem. Ind. 1891, p. 300) describes a cooling-arrangement practically identical with that described in the text as carried out by Dr. Stahl; and he gives details concerning its function. The acid travels altogether about 1000 feet, and its temperature is brought down from 139° or 149° C. to 28° or 39° C. Further on (p. 304) he contends that such cooling is unnecessary (except, perhaps, in order to save the lead from quick corrosion), as in a number of small-scale experiments he found acid of 150° Tw. at 100° C. to absorb N₂O₃ almost [but never quite!] as well as at the ordinary temperature. [Those experiments are certainly not conclusive, since Crowder carried the absorption only to 0.47 or at most 0.69 per cent. N₂O₃, and the inferior absorbing-power of hot acid would evidently come into play when acids richer in N₂O₃ were obtained; compare my experiments on the nitrous tension of sulphuric acids, pp 895 *et seq.* We cannot, therefore, abandon as yet the otherwise universal opinion that the acid intended for feeding the Gay-Lussac tower should be cooled as much as possible.]

To p. 555. *Working the Gay-Lussac tower.*—Crowder (J. Soc. Chem. Ind. 1891, p. 303) gives a table of averages of the amount of acids contained in the gases both on entering and on leaving the Gay-Lussac tower. The gases on entering contain from 3 to 4 grains of acidity per cubic foot, reckoned as SO₃ (but in reality consisting of SO₂, H₂SO₄ in the shape of mist and nitrogen acids), on leaving only about 1 or 2 grains. He believes that, if the gases contain more than that, it indicates that sulphur dioxide gets into the absorbing-tower, the result being a reduction of

nitrous acid and loss of nitre. On principle this is, of course, correct (comp. p. 558), but it is not certain whether the above amount is the real limit in all ordinary cases. Crowder also observed that the proportion of oxygen in the gases passing out of the tower is always slightly larger (0.08 to 0.54 per cent.) than that passing in. The explanation for this phenomenon proposed by him, viz. the diminution of volume consequent upon the removal of SO_2 or some decomposition of the oxides of nitrogen, is altogether inadmissible; any chemical action of the SO_2 and the nitrogen oxides within the Gay-Lussac tower could only tend to diminish, not to increase the amount of oxygen, and the shrinkage caused by the removal of those gases is far too slight to be observed in gas-analysis (it is, of course, useless to expect such gas-tests to give accurate results, even in the first decimal per cent.). I have little doubt that Crowder's observation was due to some air being drawn into the exit-tube by a slight leak or by the feeding-holes sucking in a little air; this is extremely probable, as the Gay-Lussac tower offers a very great resistance to the draught, and the inward suction at the exit-tube, as shown by an air-gauge, is consequently many times larger than that at the inlet-tube.



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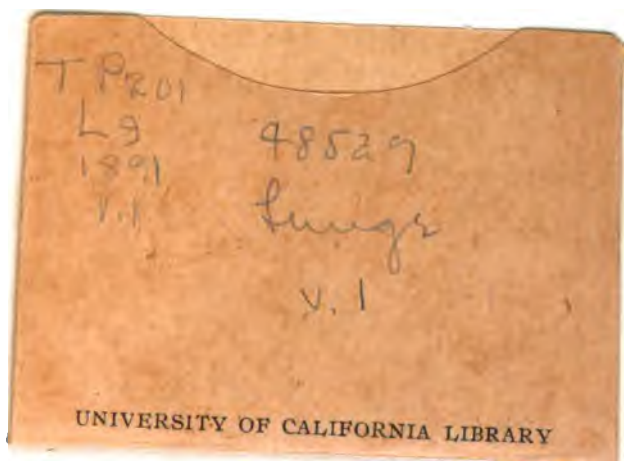
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